Supporting Information
for

Stille vs. Suzuki – Cross-Coupling for the Functionalization of Diazocines

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General Information

For reactions under inert conditions, a nitrogen filled glovebox (Pure Lab^{HE} from Inert, Amesbury, MA USA) and standard Schlenk techniques were used.

Stannylation reactions were performed in high pressure vessels using an Emrys Optimizer (Biotage, Uppsala, Sweden) or a Biotage Initiator+ SP wave (Biotage, Uppsala, Sweden) in the organic synthesis mode.

All glassware was dried in an oven at 200 °C for several hours prior to use. NMR tubes were dried in an oven at 110 °C for several hours prior to use.

NMR spectra were recorded on a Bruker Avance Neo 600 (Bruker BioSpin, Rheinstetten, Germany) (600 MHz (^{1}H), 151 MHz (^{13}C{^{1}H}), 193 MHz (^{11}B{^{1}H}), 565 MHz (^{19}F), 224 MHz (^{119}Sn{^{1}H})) or Bruker DRX 500 (500 MHz (^{1}H), 126 MHz (^{13}C{^{1}H}), 471 MHz (^{19}F)) at 298 K. All ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were referenced to the residual proton signals of the solvent (^{1}H) or the solvent itself (^{13}C{^{1}H}). ^{19}F NMR and ^{119}Sn{^{1}H} NMR spectra were referenced indirectly according to the IUPAC recommendations for the frequency ratio to ^{1}H.[1] The exact assignment of the peaks was performed by two-dimensional NMR spectroscopy such as ^{1}H COSY, ^{13}C{^{1}H} HSQC and ^{1}H/^{13}C{^{1}H} HMBC when possible.

High-resolution EI mass spectra were recorded on a MAT 95XL double-focusing mass spectrometer from Finnigan MAT (Thermo Fisher Scientific, Waltham, MA, USA) at an ionization energy of 70 eV. Samples were measured by a direct inlet method with a source temperature of 200 °C. High-resolution ESI and APCI mass spectra were measured by a direct inlet method on an Impact II mass spectrometer from Bruker Daltonics (Bruker Daltonics, Bremen, Germany). ESI mass spectra were recorded in the positive ion collection mode.

IR spectra were recorded on a Nicolet i510 FT-IR spectrometer from Thermo Fisher Scientific (Thermo Fisher Scientific, Waltham, MA, USA) with a diamond window in an area from 500 – 4000 cm^{-1} with a resolution of 4 cm^{-1}. All samples were measured 16 times against a background scan.

Melting points were recorded on a Büchi Melting Point M-560 (Büchi, Essen, Germany) and are reported corrected.

Thin layer chromatography (TLC) was performed using TLC Silica gel 60 F_{254} from Merck (Merck, Darmstadt, Germany) and compounds were visualized by exposure to UV light at a wavelength of 254 nm. Column chromatography was performed either manually using silica gel 60 (0.015-0.040 mm) from Merck (Merck, Darmstadt, Germany) or by using a PuriFlash 4250 column machine (Interchim, Mannheim, Germany). Silica gel columns of the type CHROMABOND Flash RS 15 SPHERE SiOH 15 µm (Macherey-Nagel, Düren, Germany) and PF-15SiHP-F0040, PF-50SiHP-JP-F0080, PF-50SiHP-JP-F0120 (Interchim, Mannheim, Germany) were used. The sample was applied via dry load with Celite® 503 (Macherey-Nagel, Düren, Germany) as column material. If stated, Celite® 503 (Macherey-Nagel, Düren, Germany) was used as filtration aid.

The use of abbreviations follows the conventions from the ACS Style guide.[2]

Reagents

All chemicals were commercially available and used without purification unless stated otherwise.

Table S1. List of supplier and purity of used chemicals.

Reagent	Supplier	Purity	Comments
(1,1'-Bis(diphenylphosphino)ferrocene)palladium(II) dichloride	Abcr	99.9%	Stored in a glovebox
1-Bromo-2-isopropylbenzene	BLD Pharmatech	99.30%	
1-Bromo-2-nitrobenzene	Apollo	98%	
1-Bromo-3-isopropylbenzene	BLD Pharmatech	95%	
1-Bromo-3-nitrobenzene	TCI	>98%	
1-Bromo-4-isopropylbenzene	BLD Pharmatech	96.35%	
1-Bromo-4-nitrobenzene	Acros Organics	99%	
2,2'-Ethylenedianiline	TCI	>98%	
2-Bromomesitylene	Alfa Aesar	99%	
2-Bromothiophene	Alfa Aesar	98+%	
3,5-Bis-(trifluoromethyl)-bromobenzene	Abcr	98%	
3-Bromothiophene	Alfa Aesar	97%	
4-Bromoacetophenone	Alfa Aesar	98%	
4-Bromoaniline	Sigma Aldrich	97%	
4-Bromoanisole	Abcr	99%	
4-Bromobenzonitrile	Alfa Aesar	98%	
4-Bromo-*N*,*N*-dimethylaniline	BLD Pharmatech	99.97%	
4-Bromophenol	Acros Organics	97%	
(4-Bromophenyl)diphenylamine	BLD Pharmatech	98%	
4-Bromopyridine hydrochloride	BLD Pharmatech	95%	
4-Bromotoluene	Abcr	98%	
4-Iodo-2-nitrotoluene	Apollo	98%	
5-Bromobenzo[d][1,3]dioxole	BLD Pharmatech	98.45%	
5-Bromofuran-2-carbaldehyde	BLD Pharmatech	98%	
Allyl bromide	Acros Organics	99%	Stabilized with 300 ppm propylene oxide
Bis(pinacolato)diboron	Abcr	98%	
Bromine	Acros	99+%	
Carbon	J.T.Baker	90-100%	Activated
Cesium fluoride	Abcr	99%	Stored in a glovebox
2-Dicyclohexylphosphino-2′,4′,6′-triisopropyl-biphenyl (XPhos)	BLD Pharm	97%	
Hexamethyldistannane	Acros	99%	Stored in a glovebox

Hydrazine monohydrate	Fisher	≥99%	
Iron(III) chloride hexahydrate	Sigma Aldrich	97%	
Magnesium sulfate	VWR		Dried
meta-Chloroperoxybenzoic acid	Acros	70 – 75%[1]	
Methyl 4-bromobenzoate	BLD Pharmatech	97.85%	
Methyl 5-bromofuran-2-carboxylate	BLD Pharmatech	97.88%	
N-Iodosuccinimide	Apollo	98%	Stored in a fridge
Palladium acetate	Carbolution	98%	
Potassium carbonate	Acros Organics	99+%	For analysis, anhydrous
Potassium hydroxide	Honeywell	≥85%	Pellets
Potassium *tert*-butoxide	TCI	≥97.0%	Stored in a glovebox
Sodium chloride	Th. Geyer	min 99.0%	
Sodium hydrogen carbonate	VWR	ACS, Reag. Ph. Eur.	
Sodium sulfate	Merck	≥99.0%	anhydrous

Solvents

All solvents for purification and extraction were used as received. All solvents used for synthesis under inert conditions were dried by a solvent purification system (SPS) from Inert Technologies.

Table S2. List of supplier and purity of used solvents.

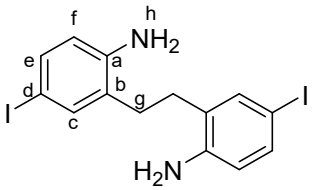
Solvent	**Supplier**	**Purity**	**Comments**
1,2-Dimethoxyethane	J&K	99.5%	SuperDry, water ≤ 30 ppm, J&KSeal
1,4-Dioxane	Acros Organics	99.5%	Extra dry, over molecular sieve, stabilized, AcroSeal™
Acetic Acid	Merck	≥99.8%	
Chloroform-d_1	Euroisotop	99.8%	
Cyclohexane	Merck	≥99.5%	
DCM	Merck	≥99.9%	
DMSO	VWR	technical grade	
DMSO	Acros Organics	99.7%	Extra dry, AcroSeal™
DMSO-d_6	Sigma Aldrich	99.9%	
Ethyl acetate	Merck	≥99.5%	
Methanol	VWR	≥99.8%	
Tetrahydrofuran	VWR	HPLC grade	Anhydrous from SPS, stored in a glovebox
Tetrahydrofuran	Fisher Scientific	≥99.8%	
Toluene	Merck	≥99.7%	Anhydrous from SPS, stored in a glovebox
Water		deionized	

[1] The exact concentration was determined by iodometric titration against sodium thiosulfate.

Syntheses

Syntheses of iodinated precursors

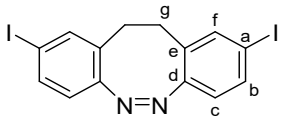
2,2'-(Ethane-1,2-diyl)bis(4-iodoaniline)[3]



Compound **2*p*** was synthesized according to a literature procedure. The analytical data are consistent with the literature.[3]

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.34 – 7.30 (m, 4H, *H*-e/f), 6.48 – 6.44 (m, 2H, *H*-c), 3.64 (s, br, 4H, *H*-h), 2.69 (s, 4H, *H*-g) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 144.2 (*C*-a), 138.0 (*C*-f), 136.2 (*C*-e), 128.6 (*C*-b), 118.1 (*C*-c), 80.3 (*C*-d), 30.6 (*C*-g) ppm.
IR (ATR): $\tilde{\nu}$ = 3397 (m, br), 3317 (m), 3219 (w), 2882 (w), 2359 (w), 1626 (m), 1562 (w), 1486 (s), 1470 (m), 1436 (m), 1398 (m), 1297 (s), 1268 (s), 1142 (m), 1096 (m), 1052 (m), 1002 (m), 931 (m), 868 (m), 834 (m), 809 (s), 709 (s) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{14}H_{14}I_2N_2]^+$ 463.92410; found 463.92397, 232.0 (100).
Mp: 165 °C.
R_f = 0.57 (*n*-hexane/DCM 1/1).

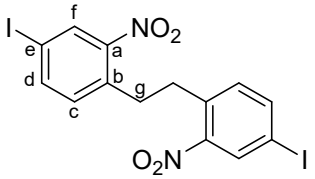
(*Z*)-2,9-Diiodo-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine[3] (**1**)



Compound **1** was synthesized according to literature procedure. The analytical data are consistent with the literature.[3]

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.48 (dd, ^3J = 8.3 Hz, ^4J = 1.8 Hz, 2H, *H*-b), 7.36 (ad, ^4J = 1.8 Hz, 2H, *H*-f), 6.59 (d, ^3J = 8.3 Hz, 2H, *H*-c), 2.97 – 2.62 (m, 4H, *H*-g) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 154.9 (*C*-d), 138.5 (*C*-f), 136.1 (*C*-b), 130.1 (*C*-e), 120.9 (*C*-c), 92.4 (*C*-a), 31.3 (*C*-g) ppm.
IR (ATR): $\tilde{\nu}$ = 2921 (w), 2358 (w), 1575 (m), 1533 (w), 1467 (m), 1383 (w), 1280 (w), 1156 (m), 1097 (m), 1052 (w), 1002 (m), 979 (w), 959 (w), 918 (w), 891 (m), 878 (m), 801 (s), 714 (m) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{14}H_{10}I_2N_2]^+$ 459.89280; found 459.89287, 178.1 (100).
Mp: 173 °C.
R_f = 0.60 (*n*-hexane/DCM 3/1).

5-Iodo-2-(4-iodo-2-nitrophenethyl)aniline[4]

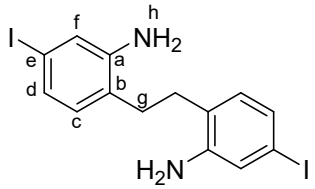


This reaction was not performed under inert conditions.

t-BuOK (5.61 g, 50.0 mmol, 1.00 equiv) was added at 0 °C to a solution of 4-iodo-2-nitrotoluene (13.2 g, 50.0 mmol, 1.00 equiv) in THF (300 mL) and the solution was stirred for 1 min. Then, bromine (2.56 mL, 7.99 g, 50.0 mmol, 1.00 equiv) was added and the mixture was stirred for 10 min at 0 °C. The reaction mixture was poured into ice (1 L). The precipitate was filtered, washed with water (400 mL) and cyclohexane (400 mL) and subsequently dried under reduced pressure yielding **3** as a yellow solid (11.1 g, 21.2 mmol, 85%, Lit.[4]:31%[2]).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.28 (ad, ^4J = 1.8 Hz, 2H, *H*-f), 7.86 (dd, ^3J = 8.1 Hz, ^4J = 1.8 Hz, 2H, *H*-d), 7.14 (d, ^3J = 8.1 Hz, 2H, *H*-c), 3.16 (s, 4H, *H*-g) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 149.6 (*C*-a), 142.4 (*C*-d), 135.4 (*C*-b), 134.1 (*C*-e), 133.6 (*C*-f), 91.1 (*C*-c), 34.1 (*C*-g) ppm.
IR (ATR): $\tilde{\nu}$ = 3079 (w), 2847 (br, w), 1517 (s), 1471 (m), 1336 (s), 1172 (w), 1130 (w), 1068 (m), 890 (m), 868 (m), 837 (s), 794 (s), 761 (s), 741 (m) cm^{-1}.
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $[C_{14}H_{10}I_2N_2O_4 + Na]^+$ 546.86222; found 546.86133.
Mp: 212 °C.
R_f = 0.80 (cyclohexane/DCM 1/3).

6,6'-(Ethane-1,2-diyl)bis(3-iodoaniline)



This reaction was not performed under inert conditions.

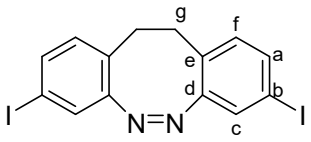
1,2-Bis(4-iodo-2-nitrophenyl)ethane (**3**) (5.24 g, 10.0 mmol, 1.00 equiv), activated carbon (444 mg, 37.0 mmol, 3.70 equiv) and $FeCl_3 \times 6\ H_2O$ (32.4 mg, 120 µmol, 1.2 mol%) were dissolved in methanol (150 mL) and stirred for 10 min at 65 °C. Hydrazine monohydrate (4.85 mL, 103 mmol, 10.0 equiv) was added and the reaction mixture was stirred for 18 h at 65 °C. After cooling down to 23 °C, the reaction mixture was filtered through Celite®. The solvent was removed under reduced pressure yielding **2*m*** as a pale-yellow solid (3.87 g, 8.35 mmol, 83%, Lit.[5]:48%[3]).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.03 (dd, ^3J = 7.9 Hz, ^4J = 1.8 Hz, 2H, *H*-d), 7.01 (ad, ^4J = 1.8 Hz, 2H, *H*-f), 6.71 (d, ^3J = 7.9 Hz, 2H, *H*-c), 3.59 (s, br, 4H, *H*-h), 2.70 (s, 4H, *H*-g) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 145.9 (*C*-a), 131.3 (*C*-c), 128.0 (*C*-d), 125.5 (*C*-b), 124.4 (*C*-f), 92.2 (*C*-e), 30.4 (*C*-g) ppm.
IR (ATR): $\tilde{\nu}$ = 3415 (w), 3340 (w), 2882 (br, m), 2118 (br, w), 1866 (br, w), 1613 (m), 1584 (m), 1563 (m), 1485 (s), 1438 (m), 1401 (m), 1265 (m), 1181 (m), 1084 (m), 938 (w), 871 (m), 854 (m), 813 (s), 775 (m) cm^{-1}.

[2] In this report, air was used as oxidant.
[3] In this report, tin(II) chloride hexahydrate was used as reducing agent.

HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{14}H_{14}I_2N_2]^+$ 463.92410; found 463.92399, 231.9 (100).
Mp: 160 °C.
$\mathbf{R_f}$ = 0.37 (*n*-hexane/DCM 1/1).

(*Z*)-3,8-Diiodo-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**2**)



This reaction was not performed under inert conditions.

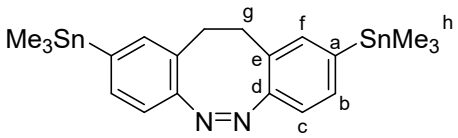
A freshly prepared solution of *m*CPBA (70%, 2.47 g, 14.3 mmol, 2.00 equiv) in acetic acid (20 mL) was added dropwise over the course of 2 h under rapid stirring to a solution of a 2,2'-ethylenedi(3-iodoaniline) (**2*m***) (2.32 g, 5.00 mmol, 1.00 equiv) in acetic acid (30 mL) and DCM (90 mL). After the complete addition of the *m*CPBA solution, the mixture was stirred for further 16 h at 25 °C. Then, the solvent was removed under reduced pressure. The residue was re-dissolved in DCM (50 mL) and washed with an aqueous solution of sodium hydrogen carbonate (2 M, 3 × 50 mL). The combined organic phases were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was purified via column chromatography on silica (eluent: cyclohexane/DCM 1/3) to afford **2** as a yellow solid (855 mg, 1.86 mmol, 37%, Lit.[5]: 35%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.36 (dd, ^3J = 8.1 Hz, ^4J = 1.8 Hz, 2H, *H*-a), 7.19 (ad, ^4J = 1.8 Hz, 2H, *H*-c), 6.73 (d, ^3J = 8.1 Hz, 2H, *H*-f), 2.94 – 2.66 (m, 4H, *H*-g) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 156.1 (*C*-d), 136.5 (*C*-a), 131.6 (*C*-f), 127.7 (*C*-e), 127.6 (*C*-c), 91.4 (*C*-b), 31.3 (*C*-g) ppm.
IR (ATR): $\tilde{\nu}$ = 3037 (w), 1577 (m), 1552 (m), 1462 (m), 1376 (m), 1258 (w), 1158 (w), 1090 (m), 975 (w), 882 (m), 820 (s), 798 (s), 721 (m) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{14}H_{10}I_2N_2]^+$ 459.89280; found 459.89334, 178.0 (100).
Mp: 184 °C.
$\mathbf{R_f}$ = 0.66 (cyclohexane/DCM 1/3).

General Procedure for the Stille-Kelly Cross-Coupling Reaction

Under inert conditions, the corresponding di-iodinated diazocine (345 mg, 750 µmol, 1.00 equiv), hexamethyldistannane (573 mg, 1.75 mmol, 2.33 equiv) and $[Pd(PPh_3)_4]$[6] (34.8 mg, 30.0 µmol, 4 mol%) were dissolved in toluene (2.5 mL) and THF (2.5 mL) in a microwave reaction vessel. The reaction mixture was stirred for 10 min at 150 °C under microwave irradiation and subsequently filtered through Celite®. Then, the solvent and excess hexamethyldistannane were removed under reduced pressure (9.5×10^{-2} mbar, 80 °C). The residue was purified via column chromatography on silica.

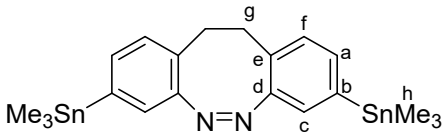
(*Z*)-2,9-Bis(trimethylstannyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**3**)



Compound **3** was synthesized according to the general procedure from (*Z*)-2,9-diiodo-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**1**). The product **3** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM 1/2) as a yellow solid (326 mg, 612 µmol, 82%). The reaction was repeated on a 3.00 mmol scale yielding **3** in 77% (1.23 g, 2.31 mmol).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.26 (d, ^3J = 7.5 Hz, 2H, *H*-b), 7.10 (s, 2H, *H*-f), 6.84 (d, ^3J = 7.5 Hz, 2H, *H*-c), 3.02 – 2.73 (m, 4H, *H*-g), 0.23 (s, 18H, *H*-h) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 155.6 (*C*-d), 141.3 (*C*-a), 137.2 (*C*-f), 134.1 (*C*-b), 127.2 (*C*-e), 118.6 (*C*-c), 32.0 (*C*-g), -9.3 (*C*-h) ppm.
^{z119}Sn{^{1}H} NMR (224 MHz, $CDCl_3$) δ = -25.55 ppm.
IR (ATR): $\tilde{\nu}$ = 2987 (w), 2907 (w), 2359 (w), 1703 (w), 1524 (w), 1457 (w), 1429 (w), 1374 (w), 1183 (w), 1068 (w), 948 (w), 922 (w), 891 (w), 833 (w), 763 (s), 711 (m) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{20}H_{28}N_2{}^{120}Sn_2]^+$ 536.02909; found 536.03099, 490.8 (100).
Mp: 139 °C.
R_f = 0.46 (cyclohexane/DCM 2/1).

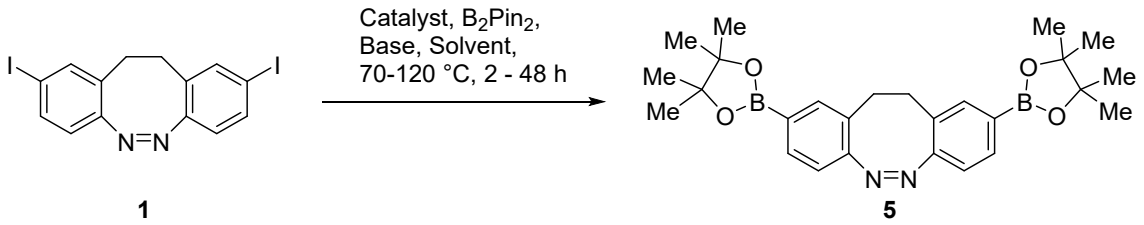
(*Z*)-3,8-Bis(trimethylstannyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**4**)



Compound **4** was synthesized according to the general procedure from (*Z*)-3,8-diiodo-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**2**). The product **4** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM 1/2) as a yellow solid (281 mg, 527 µmol, 70%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.12 (dd, ^3J = 7.4 Hz, ^4J = 1.0 Hz, 2H, *H*-a), 6.94 (d, ^3J = 7.4 Hz, 2H, *H*-f), 6.94 (ad, ^4J = 1.0 Hz, 2H, *H*-c), 3.01 – 2.69 (m, 4H, *H*-g), 0.22 (s, 18H, *H*-h) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 155.4 (*C*-d), 140.6 (*C*-b), 134.5 (*C*-a), 129.1 (*C*-f), 128.1 (*C*-e), 125.9 (*C*-c), 31.9 (*C*-g), -9.4 (*C*-h) ppm.
^{119}Sn{^{1}H} NMR (224 MHz, $CDCl_3$) δ = -23.71 ppm.
IR (ATR): $\tilde{\nu}$ = 2912 (w, br), 1514 (w), 1434 (w), 1366 (w), 1261 (w), 1186 (m), 1073 (m), 984 (w), 954 (w), 922 (w), 887 (m), 858 (w), 820 (m), 799 (m), 764 (s), 714 (s) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{20}H_{28}N_2{}^{120}Sn_2]^+$ 536.03001; found 536.03073, 490.8 (100).
Mp: 103 °C.
R_f = 0.43 (cyclohexane/DCM 2/1).

Optimization of the Miyaura Borylation



1 **5**

Table S3. Optimization of the Miyaura Borylation of **1**.

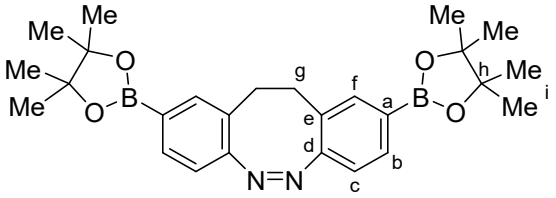
Entry	mmol	Base [4 eq]	Catalyst [5mol%]	B_2pin_2 [eq]	Solvent	T [°C]	Time [h]	Yield [%]
1	0.2	KOAc	$Pd(dppf)Cl_2$	3.00	DMSO	100	16	65
2	0.2	KOAc	$Pd(acac)_2$	3.00	DMSO	100	16	26
3	0.2	KOAc	$Pd(PPh_3)_4$	3.00	DMSO	100	16	52
4	0.2	KOAc	$Pd(PPh_3)_4$	3.00	DMSO	100	48	43
5	0.2	*t*-BuOK	$Pd(dppf)Cl_2$	3.00	DMSO	100	16	0
6	0.2	K_3PO_4	$Pd(dppf)Cl_2$	3.00	1,4-Dioxan	100	16	0
7	0.2	K_3PO_4	$Pd(dppf)Cl_2$	3.00	DMSO	100	16	14
8	0.2	K_3PO_4	$Pd(dppf)Cl_2$	3.00	1,4-Dioxan / Water (10:1)	100	16	Traces
9	0.2	KOAc	$Pd(dppf)Cl_2$	3.00	1,4-Dioxan	100	16	Traces
10	0.2	KOAc	$Pd(dppf)Cl_2$	3.00	1,4-Dioxan / Water (10:1)	100	16	10
11	1.0	KOAc	$Pd(dppf)Cl_2$	3.00	DMSO	70	16	27
12	1.0	KOAc	$Pd(dppf)Cl_2$	3.00	DMSO	90	16	63
13	1.0	KOAc	$Pd(dppf)Cl_2$	3.00	DMSO	120	16	13
14	1.0	KOAc	$Pd(dppf)Cl_2$	2.60	DMSO	100	16	66
15	1.0	KOAc	$Pd(dppf)Cl_2$	2.80	DMSO	100	16	70
16	1.0	KOAc	$Pd(dppf)Cl_2$	2.80	DMSO	100	2[4]	91
17	1.0	KOAc	$Pd(dppf)Cl_2$	2.80	DMSO	90	4[4]	86

General Procedure for the Miyaura Borylation

Under inert conditions, the corresponding di-iodinated diazocine (1.00 equiv), $Pd(dppf)Cl_2$ (5 mol%), B_2Pin_2 (2.80 equiv) and KOAc (4.00 equiv) were dissolved in DMSO (10 mL/mmol). The mixture was stirred at 100 °C and the reaction progress was monitored by TLC (cyclohexane/DCM/ethyl acetate 55/40/5). After completion (approx. 2 h), the reaction mixture was diluted with ethyl acetate (20 mL/mmol) and washed with brine (4 × 50 mL/mmol). The organic phase was dried over sodium sulfate, filtered and the solvent removed *in vacuo*. The residue was purified by column chromatography on silica (eluent: cyclohexane/DCM/ethyl acetate 55/40/5) to obtain the corresponding diazocine as a yellow solid.

[4] Stopped after consumption of starting material. Monitored by TLC every 20 minutes.

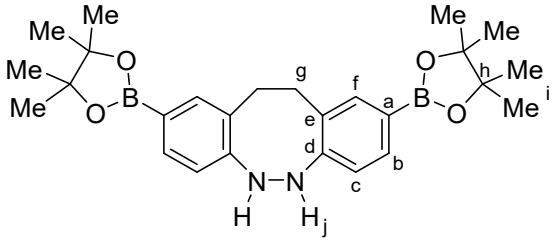
(*Z*)-2,9-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**5**)



Compound **5** was synthesized according to the general procedure from (*Z*)-3,8-diiodo-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**1**). The product **5** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM/ethyl acetate 55/40/5) as a yellow solid (419 mg, 910 µmol, 91%). The reaction was repeated on a 4.00 mmol scale yielding **5** in 82%.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.55 (dd, ^3J = 7.8 Hz, ^4J =1.1 Hz, 2H, *H*-b), 7.40 (d, ^4J = 1.1 Hz, 2H, *H*-f), 6.8 (d, ^3J = 7.8 Hz, 2H, *H*-c), 2.98 - 2.78 (m, 4H, *H*-g), 1.30 (d, ^3J = 5.7 Hz, 24H, *H*-j) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) *δ* = 158.0 (*C*-d), 136.6 (*C*-f), 133.3 (*C*-b), 127.3 (*C*-e), 118.1(*C*-c), 84.0 (*C*-h), 31.6 (*C*-g), 25.1 (*C*-i), 25.0 (*C*-i) ppm.[5]
^{11}B{^{1}H}NMR (193 MHz, $CDCl_3$) *δ* 31.0 ppm.
IR (ATR): $\tilde{\nu}$ = 2977 (w, br), 1605 (w), 1485 (w), 1468 (w), 1408 (w), 1389 (m), 1354 (s), 1327 (m), 1278 (m), 1210 (w), 1166 (w), 1139 (s), 1118 (m), 1108 (s), 1013 (w), 992 (w), 964 (m), 909 (w), 848 (s), 832 (m), 811 (w), 776 (w), 745 (w), 709 (w), 695 (w), 680 (m) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{26}H_{34}{}^{11}B_2N_2O_4]^+$ 460.27083; found 460.27096, 83.1 (100).
Mp: 275°C.
R_f = 0.60 (cyclohexane/DCM/EA 5/4/1).

2,9-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,6,11,12-tetrahydrodibenzo[c,g][1,2]diazocine



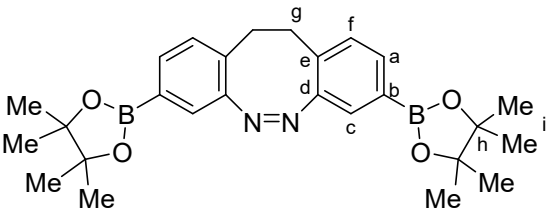
Side product 2,9-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,6,11,12-tetrahydrodibenzo[c,g][1,2]di-azocine was synthesized according to the general procedure from (*Z*)-3,8-diiodo-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**1**) with longer reaction times of 18 h. The product 2,9-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,6,11,12-tetrahydrodibenzo[c,g][1,2]di-azocine was obtained after purification via column chromatography on silica (eluent: cyclohexane/ethyl acetate 4/1) as a colourless solid (210 mg, 455 µmol, 46%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.59 (d, ^4J = 1.5 Hz, 2H, *H*-f), 7.52 (dd, ^3J = 7.7 Hz, ^3J = 1.5 Hz, 2H, *H*-b), 6.70 (d, ^3J = 7.7 Hz, 2H, *H*-c), 5.63 (s, 2H, *H*-j), 3.20 (s, 4H, *H*-g), 1.33 (s, 24H, *H*-i). ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) *δ* =149.3 (*C*-d), 137.8 (*C*-f), 133.6 (*C*-b), 132.5 (*C*-e), 122.4 (*C*-a), 116.8 (*C*-c), 83.6 (*C*-h), 31.2 (*C*-g), 25.0 (*C*-i), 24.9 (*C*-i) ppm.
^{11}B{^{1}H}NMR (193 MHz, $CDCl_3$) *δ* 31.0 ppm.
IR (ATR): $\tilde{\nu}$ = 3356(w), 2976 (w), 2920 (w), 1607 (w), 1577 (w), 1515 (w), 1470 (w), 1442 (w), 1409 (w), 1372 (m), 1349 (m), 1326 (w), 1270 (w), 1240 (w), 1216 (w), 1167(m), 1143 (m), 1131 (m), 1119 (m), 1094 (w), 1008 (w), 966 (w), 952 (w), 925 (w), 905 (w), 855 (w), 823 (w), 767 (w), 742 (w), 697 (m), 681 (m) cm^{-1}.

[5] Due to the quadrupolar relaxation of the boron nucleus *C*-b was not observed.

HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{26}H_{36}{}^{11}B_2N_2O_4]^+$ 462.28612; found 462.28613, 232.1 (100).
Mp: 218°C.
R_f = 0.43 (cyclohexane/ethyl acetate 4/1).

(*Z*)-3,8-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**6**)



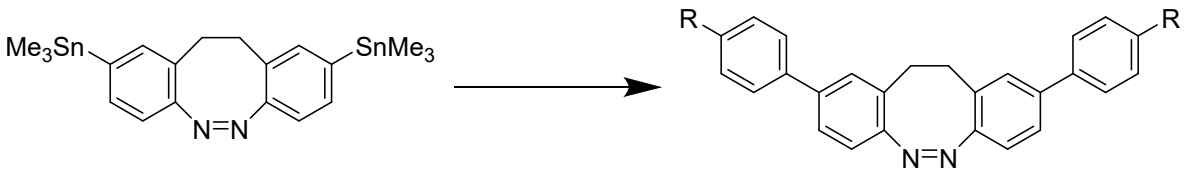
Compound **6** was synthesized according to the general procedure from (*Z*)-3,8-diiodo-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**2**). The product **6** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM/ethyl acetate 55/40/5) as a yellow solid (312 mg, 678 µmol, 68%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.43 (dd, ^3J = 7.5 Hz, ^4J = 1.2 Hz, 2H, *H*-a), 7.29 (ad, ^4J = 1.2 Hz, 2H, *H*-c), 6.98 (d, ^3J = 7.5 Hz, 2H, *H*-f), 3.02 – 2.75 (m, 4H, *H*-g), 1.30 (d, ^3J = 5.8 Hz, 24H, *H*-i) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 155.0 (*C*-d), 133.5 (*C*-a), 131.1 (*C*-e), 129.1 (*C*-f), 125.5 (*C*-c), 84.1 (*C*-h), 32.1 (*C*-g), 25.1 (*C*-h), 24.9 (*C*-h) ppm.[6]
^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ = 29.73 ppm.
IR (ATR): $\tilde{\nu}$ = 2981 (w, br), 1606 (w), 1496 (w), 1389 (m), 1357 (s), 1325 (m), 1262 (m), 1262 (w), 1211 (m), 1141 (s), 1122 (m), 1106 (s), 965 (m), 997 (w), 850 (s), 821 (m), 717 (m) cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $[C_{26}H_{35}{}^{11}B_2N_2O_4 + H]^+$ 461.27799; found 461.27800.
Mp: 282 °C.
R_f = 0.38 (cyclohexane/DCM/ethyl acetate 55/40/5).

[6] Due to the quadrupolar relaxation of the boron nucleus *C*-b was not observed.

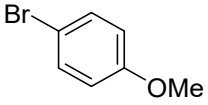
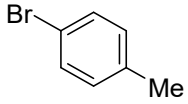
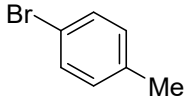
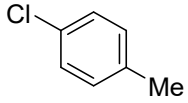
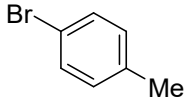
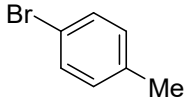
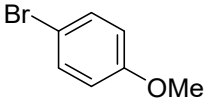
Optimization for the Stille Cross-Coupling Reaction

The Stille reaction is a well investigated cross-coupling method with many different reported reaction conditions and catalytic systems.[7] Depending on the reaction conditions, the Stille reaction proceeds via a concerted or an open reaction mechanism. The conversion of the reaction can be highly enhanced by the addition of an additive suitable for the specific mechanism. However, this additive can also hinder the reaction if the mechanism proceeds via the other pathway. Hence, the reaction conditions have to be evaluated carefully when applying the Stille reaction.[8] Although there has been a lot of progress in the reaction conditions of the Stille reaction,[7] these benefits have not been exploited to the Stille reaction on diazocines so far, i.e. no additives were used[9] or the combination of the catalytic system with the solvent and additive was not effective.[10]. As our group has a broad expertise in the Stille cross-coupling reaction, we were interested if the coupling of diazocines can be highly enhanced by an efficient combination of the catalytic system. Firstly, we applied the reaction conditions of our established protocol of the Stille reaction for stannylated azobenzenes[11] on the stannylated diazocine **3** (**Table S3**, entry 1). With the addition of CuCl and LiCl, we could obtain the product **12** in 42% yield, which is significantly lower than the yield for the corresponding azobenzene. As the reaction required a high stochiometric amount of the additives and a long reaction time, we envisioned that another catalytic system might be more efficient. Baldwin and co-workers reported a great enhancement of the Stille reaction using a combination of CuI and CsF as additives.[12] This method proceeds under mild conditions as it provides the cross-coupling products in good yields while using a low reaction temperature of only 45 °C.[12] Unfortunately, using these reaction conditions in the Stille reaction of stannylated diazocine **3** with 4-bromotoluene led to no detectable formation of the cross-coupling product **7** (entry 2). By increasing the reaction temperature to 70 °C, the desired coupling product **7** could be obtained in 70% yield (entry 3). A full conversion of stannylated diazocine **3** could not be achieved with this catalytic system and side reactions occurred that could not be further analyzed. To circumvent these side reactions, a different catalytic system was used. Buchwald and co-workers published an efficient protocol for the Stille reaction using $Pd(OAc)_2$/XPhos as catalytic system, CsF as additive and DME as solvent.[13] Compared to the previously used conditions, this method requires lower catalyst loads and fewer additives. Remarkably, they were able to couple stannylated compounds with a wide range of even chlorinated electrophilic compounds, which are less reactive than the commonly used brominated derivatives. However, the Stille reaction of the stannylated diazocine **3** and 4-chlorotoluene led to no detectable formation of the desired coupling product **7** within 4 h (entry 4). Changing the electrophilic compound to the more reactive 4-bromotoluene proved to be successful; the coupling product **7** was obtained in 94% yield (entry 5). Decreasing the amount of catalytic system and additive further, led to no significant decrease in yield (entry 6). As we could also more than double the yield of the coupling between **3** and 4-bromoanisole with these reaction conditions compared to our first attempt (entry 7), these conditions were used to investigate the scope of the Stille reaction of diazocines.



3

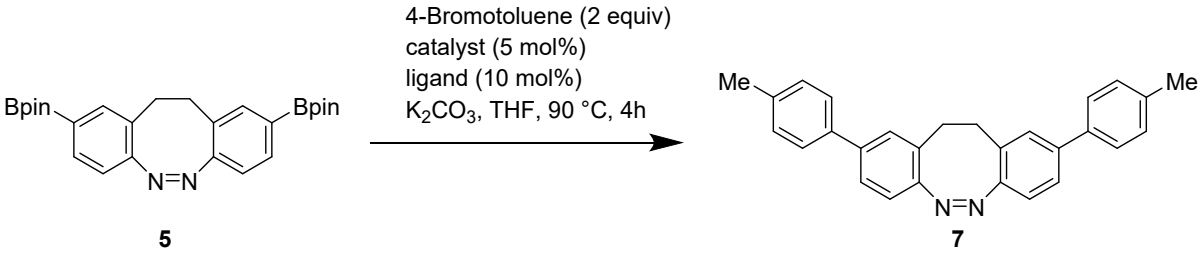
Table S4. Optimization of Stille cross-coupling reaction of stannylated diazocine **3**.

Entry	Coupling Partner	Catalytic System	Additives	Solvent	T [°C]	T [h]	Yield [%]
1	 (2.33 equiv)	$Pd(PPh_3)_4$ (4 mol%)	CuCl (6.00 equiv), LiCl (12.0 equiv)	DMF	70	65	43
2	 (2.00 equiv)	$PdCl_2$ (4 mol%), P(*t*-Bu_3)(8 mol%)	CuI (8 mol%), CsF (4.00 equiv)	DMF	45	100	--
3	 (2.00 equiv)	$PdCl_2$ (4 mol%), P(*t*-Bu_3)(8 mol%)	CuI (8 mol%), CsF (1.80 equiv)	DMF	70	19	70
4	 (2.00 equiv)	$Pd(OAc)_2$ (4 mol%), XPhos (4.4 mol%)	CsF (4.00)	DME	80	4	--
5	 (2.00 equiv)	$Pd(OAc)_2$ (4 mol%), XPhos (4.4 mol%)	CsF (4.00)	DME	80	4	94
6	 (2.00 equiv)	$Pd(OAc)_2$ (2 mol%), XPhos (2.2 mol%)	CsF (2.00)	DME	80	4	92
7	 (2.00 equiv)	$Pd(OAc)_2$ (2 mol%), XPhos (2.2 mol%)	CsF (2.00)	DME	80	4	90

General Procedure for the Stille Cross-Coupling Reaction

Under inert conditions, the corresponding di-stannylated diazocine (53.4 mg, 100 µmol, 1.00 equiv), the corresponding brominated coupling partner (200 µmol, 2.00 equiv), $Pd(OAc)_2$ (449 µg, 2.00 µmol, 2 mol%), XPhos (1.05 mg, 2.20 µmol, 2.2 mol%) and CsF (30.4 mg, 200 µmol, 2.00 equiv) were dissolved in dry DME (2 mL) in a pressure reaction vial. The mixture was stirred at 80 °C for 24 h. After cooling to 23 °C, the reaction mixture was filtered through Celite® and the solvent was removed under reduced pressure.

Optimization and General Procedure for the Suzuki Cross-Coupling Reaction



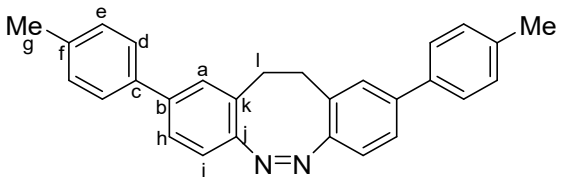
5 **7**

Table S5. Optimization of Suzuki cross-coupling reaction of borylated diazocine **5**.

Catalyst	Ligand	Yield (%)
$Pd(PPh_3)_4$		35
$Pd(ddpf)_2Cl_2$	-	39
$Pd(OAc)_2$	-	53
$Pd(OAc)_2$	XantPhos	54
$Pd(OAc)_2$	BrettPhos	51
$Pd(OAc)_2$	SPhos	86
$Pd(OAc)_2$	XPhos	91

Under inert conditions, the corresponding di-borylated diazocine **5** (46.0 mg, 100 µmol, 1.00 equiv), $Pd(OAc)_2$ (1.12 mg, 5 µmol, 5 mol%), XPhos (4.77 mg, 10.0 µmol, 10 mol%), K_2CO_3 (69.11 mg, 500 µmol, 5.00 equiv) and the corresponding brominated coupling partner (200 µmol, 2.00 equiv) were dissolved in THF (5 mL) and sealed in a pressure reaction vial. The mixture was stirred at 90 °C for 18 h. After cooling to 23 °C, the reaction mixture was filtered through Celite® and the solvent was removed under reduced pressure.

(*Z*)-2,9-Di-*p*-tolyl-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**7**)



Stille cross-coupling reaction:

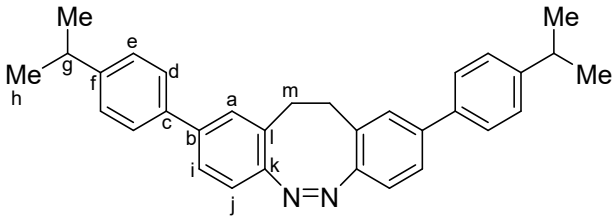
Compound **7** was synthesized according to the general procedure from 4-bromotoluene (34.2 mg, 200 µmol) with a reaction time of 4 h. The product **7** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM 1/2) as a yellow solid (35.6 mg, 91.6 µmol, 92%).

Suzuki cross-coupling reaction:

Compound **7** was synthesized according to the general procedure from 4-bromotoluene (34.2 mg, 200 µmol). The product **7** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM 3/2) as a yellow solid (35.2 mg, 90.6 µmol, 91%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.39 (d, ^3J = 8.3 Hz, 2H, *H*-d), 7.37 (dd, ^3J = 8.1 Hz, ^4J = 1.9 Hz, 2H, *H*-h), 7.21 (ad, ^4J = 1.9 Hz, 2H, *H*-a), 7.18 (d, ^3J = 8.3 Hz, 4H, *H*-e), 6.96 (d, ^3J = 8.1 Hz, 2H, *H*-i), 2.97 (s, 4H, *H*-l), 2.35 (s, 6H, *H*-g) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 154.5 (*C*-j), 140.1 (*C*-b), 137.4 (*C*-f), 137.3 (*C*-c), 129.6 (*C*-e), 128.5 (*C*-k), 128.2 (*C*-a), 126.9 (*C*-d), 125.4 (*C*-h), 119.9 (*C*-i), 32.2 (*C*-l), 21.2 (*C*-g) ppm.
IR (ATR): $\tilde{\nu}$ = 2914 (w), 1601 (w), 1515 (m), 1478 (m), 1462 (w), 1389 (w), 1184 (w), 1112 (w), 898 (m), 837 (w), 811 (s), 797 (s), 714 (w) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{28}H_{24}N_2]^+$ 388.19340; found 388.19379, 360.0 (100).
Mp: 192 °C**.**
R$_f$: 0.62 (cyclohexane/DCM 1/2), 0.17 (cyclohexane/DCM 3/2)

(*Z*)-2,9-Bis(4-isopropylphenyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**8**)



Stille cross-coupling reaction:

Compound **8** was synthesized according to the general procedure from 1-bromo-4-isopropylbenzene (39.8 mg, 200 µmol) with a reaction time of 4 h. The product **8** was obtained after purification via column chromatography on silica (eluent: cyclohexane/ethyl acetate 4/1) as a yellow solid (39.9 mg, 89.7 µmol, 90%).

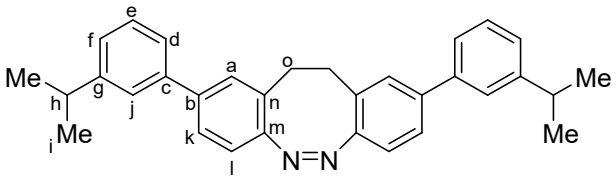
Suzuki cross-coupling reaction:

Compound **8** was synthesized according to the general procedure from 1-bromo-4-isopropylbenzene (39.8 mg, 200 µmol). The product **8** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM 3/2) as a yellow solid (37.4 mg, 84.1 µmol, 84%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.41 (d, ^3J = 8.2 Hz, 4H, *H*-d), 7.37 (dd, ^3J = 8.1 Hz, ^4J = 1.9 Hz, 2H, *H*-i), 7.24 (d, ^3J = 8.2 Hz, 4H, *H*-e), 7.21 (ad, ^4J = 1.9 Hz, 2H, *H*-a), 6.95 (d, ^3J = 8.1 Hz, 2H, *H*-j), 2.96 (s, 4H, *H*-m) , 2.91 (p, ^3J = 6.9 Hz, 2H, *H*-g) , 1.25 (d, ^3J = 6.9 Hz, 12H, *H*-h) ppm.

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 154.6 (*C*-k), 148.4 (*C*-f), 140.1 (*C*-b), 137.7 (*C*-c), 128.5 (*C*-l), 128.3 (*C*-a), 127.0 (*C*-d), 127.0 (*C*-e), 125.4 (*C*-i), 119.8 (*C*-j), 33.9 (*C*-g), 32.2 (*C*-m), 24.1 (*C*-h) ppm.
IR (ATR): $\tilde{\nu}$ = 2958 (w), 1906 (w), 1515 (w), 1478 (m), 1458 (w), 1387 (w), 1362 (w), 1302 (w), 1097 (w), 1057 (w), 1017 w), 952 (w), 900 (m), 839 (m), 821 (s), 804 (s), 740 (w), 697 (w) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{32}H_{32}N_2]^+$ 444.25600; found 444.25554, 401.0 (100).
Mp: 200 °C**.**
R_f: 0.47 (cyclohexane/ethyl acetate 4/1), 0.23 (cyclohexane/DCM 3/2).

(*Z*)-2,9-Bis(3-isopropylphenyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**9**)



Stille cross-coupling reaction:

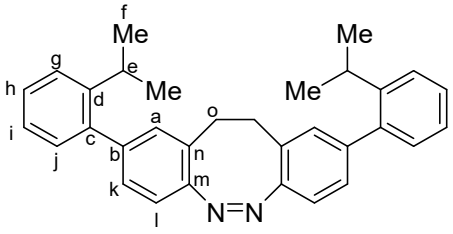
Compound **9** was synthesized according to the general procedure from 1-bromo-3-isopropylbenzene (39.8 mg, 200 µmol) with a reaction time of 4 h. The product **9** was obtained after purification via column chromatography on silica (eluent: cyclohexane/ethyl acetate 4/1) as a yellow solid (41.1 mg, 93.1 µmol, 93%).

Suzuki cross-coupling reaction:

Compound **9** was synthesized according to the general procedure from 1-bromo-3-isopropylbenzene (39.8 mg, 200 µmol). The product **9** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM 3/2) as a yellow solid (36.5 mg, 82.1 µmol, 82%).

^1H NMR (600 MHz, $CDCl_3$) δ = 7.40 (dd, ^3J = 8.2 Hz, ^4J = 1.9 Hz, 2H, *H*-k), 7.34 (s, 2H, *H*-j), 7.31 (d, ^3J = 5.2 Hz, 4H, *H*-d, e), 7.24 (ad, ^4J = 1.9 Hz, 2H, *H*-a), 7.20 – 7.16 (m, 2H, *H*-f), 6.97 (d, ^3J = 8.2 Hz, 2H, *H*-l), 3.13 – 2.85 (m, 6H, *H*-h, o), 1.26 (d, ^3J = 7.0 Hz, 12H, *H*-i) ppm.
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 154.7 (*C*-m), 149.6 (*C*-g), 140.4 (*C*-b), 140.2 (*C*-c), 128.9 (*C*-e), 128.5 (*C*-a), 128.5 (*C*-n), 125.7 (*C*-k), 125.7 (*C*-f), 125.3 (*C*-j), 124.6 (*C*-d), 119.8 (*C*-l), 34.4 (*C*-h), 32.2 (*C*-o), 24.2 (*C*-i) ppm.
IR (ATR): $\tilde{\nu}$ = 3022 (w), 2956 (m), 1732 (w), 1600 (m), 1515 (w), 1473 (m), 1460 (m), 1431.7 (w), 1383 (w), 1362 (w), 1330 (w), 1259 (w), 1171 (w), 1097 (w), 1048 (w), 999 (w), 887 (m), 830 (m), 789 (s), 702 (s), 667 (w) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{32}H_{32}N_2]^+$ 444.25600; found 444.25576, 416.0 (100).
Mp: 101 °C**.**
R_f: 0.52 (cyclohexane/ethyl acetate 4/1), 0.13 (cyclohexane/DCM 3/2).

(*Z*)-2,9-Bis(2-isopropylphenyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**10**)



Stille cross-coupling reaction:

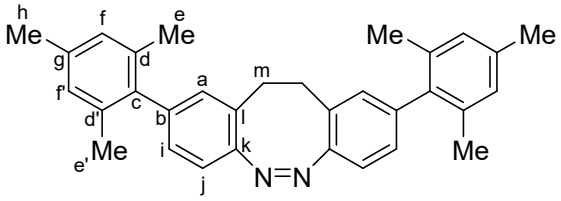
Compound **10** was synthesized according to the general procedure from 1-bromo-2-isopropylbenzene (39.8 mg, 200 µmol) using pre-milled $Pd(OAc)_2$/XPhos (1:3 ratio, 16.5 mg, 10.0 µmol, 10 mol%). The reaction mixture was stirred for 3 d at 80 °C. The product **10** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM 1/1) as a yellow solid (38.2 mg, 85.8 µmol, 86%).

Suzuki cross-coupling reaction:

Compound **10** was synthesized according to the general procedure from 1-bromo-2-isopropylbenzene (39.8 mg, 200 µmol). The product **10** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM 3/2) as a yellow solid (26.8 mg, 60.2 µmol, 60%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (dd, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 2H, *H*-g), 7.31 (ddd, ^3J = 7.9 Hz, ^3J = 7.4 Hz, ^4J = 1.4 Hz, 2H, *H*-h), 7.16 (ddd ^3J = 7.4, ^3J = 7.3 Hz, ^4J = 1.5 Hz, 2H, *H*-i), 7.11 (dd, ^3J = 6.2 Hz, ^4J = 1.8 Hz, 2H, *H*-k), 7.02 (dd, ^3J = 7.3 Hz, ^4J = 1.4 Hz 2H, *H*-j), 6.93 (d, ^4J = 1.8 Hz 2H, *H*-a), 6.92 (d, ^3J = 6.2 Hz, 2H, *H*-l), 3.11 - 2.75 (m, 4H, *H*-o), 2.94 – 2.88 (m, 2H, *H*-e), 1.11 (d, ^3J = 8.2 Hz, 12H, *H*-f) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 154.5 (*C*-k), 146.4 (*C*-d), 141.1 (*C*-b), 140.2 (*C*-c), 130.5 (*C*-a), 129.9 (*C*-j), 128.1 (*C*-n), 128.0 (*C*-g), 127.7 (*C*-k), 125.7 (*C*-h), 125.4 (*C*-i), 118.7 (*C*-l), 32.0 (*C*-o), 29.4 (*C*-e), 24.3 (*C*-f), 24.2 (*C*-f) ppm.
IR (ATR): $\tilde{\nu}$ = 2960 (m, br), 1474 (m), 1345 (w), 1085 (w), 1043 (w), 909 (m), 832 (m), 816 (w), 756 (s), 741 (s) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{32}H_{32}N_2]^+$ 444.25600; found 444.25363, 444.0 (100).
Mp: 141 °C**.**
R_f: 0.22 (cyclohexane/DCM 1/1), 0.17 (cyclohexane/DCM 3/2).

(*Z*)-2,9-Dimesityl-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**11**)



Stille cross-coupling reaction:

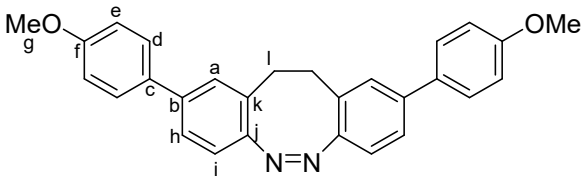
Compound **11** was synthesized according to the general procedure from 2-bromomesitylene (39.8 mg, 200 µmol) using pre-milled $Pd(OAc)_2$/XPhos (1:3 ratio, 16.5 mg, 10.0 µmol, 10 mol%). The reaction mixture was stirred for 3 d at 80 °C. The product **11** was obtained after purification via column chromatography on silica (eluent: cyclohexane → DCM) as a yellow solid (25.5 mg, 57.3 µmol, 57%).

Suzuki cross-coupling reaction:

Compound **11** was synthesized according to the general procedure from 2-bromomesitylene (39.8 mg, 200 µmol). The product **11** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM 3/2) as a yellow solid (15.7 mg, 35.3 µmol, 35%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 6.94 – 6.90 (m, 6H, *H*-i, j, f'), 6.85 (ad, ^4J = 2.0 Hz, 2H, *H*-f), 6.76 (ad, ^4J = 1.3 Hz, 2H, *H*-a), 3.13 – 2.71 (m, 4H, *H*-m), 2.29 (s, 6H, *H*-h), 2.03 (s, 6H, *H*-e), 1.64 (s, 6H, *H*-e') ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 154.4 (*C*-k), 140.1 (*C*-b), 138.2 (*C*-c), 136.9 (*C*-g), 136.1 (*C*-d), 135.9 (*C*-d'), 130.4 (*C*-a), 128.6 (*C*-l), 128.0 (*C*-f), 127.8 (*C*-f', i), 118.9 (*C*-j), 32.0 (*C*-m), 21.1 (*C*-h), 20.9 (*C*-e), 20.5 (*C*-e') ppm.
IR (ATR): $\tilde{\nu}$ = 2917 (w, br), 2109 (w), 1901 (w), 1470 (m), 1435 (m), 1376 (w), 1326 (w), 1095 (m), 1037 (m), 901 (m), 854 (s), 827 (s), 809 (s), 744 (w), 704 (w) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{32}H_{32}N_2]^+$ 444.25600; found 444.25578, 416.0 (100).
Mp: 217 °C**.**
R_f: 0.33 (cyclohexane/DCM 1/2), 0.26 (cyclohexane/DCM 3/2).

(*Z*)-2,9-Bis(4-methoxyphenyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**12**)



Stille cross-coupling reaction:

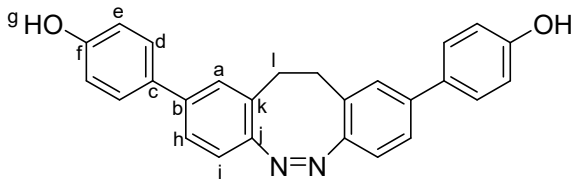
Compound **12** was synthesized according to the general procedure from 4-bromoanisole (37.4 mg, 200 µmol) with a reaction time of 4 h. The product **12** was obtained after purification via column chromatography on silica (eluent: cyclohexane/ethyl acetate 3/1) as a yellow solid (37.8 mg, 89.9 µmol, 90%).

Suzuki cross-coupling reaction:

Compound **12** was synthesized according to the general procedure from 4-bromoanisole (37.4 mg, 200 µmol). The product **12** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM/ethyl acetate 5/4/1) as a yellow solid (39.8 mg, 94.6 µmol, 95%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.43 (d, ^3J = 8.8 Hz, 4H, *H*-d), 7.34 (dd, ^3J = 8.2 Hz, ^4J = 1.9 Hz, 2H, *H*-h), 7.19 (ad, ^4J = 1.9 Hz, 2H, *H*-a), 6.95 (d, ^3J = 8.2 Hz, 2H, *H*-i), 6.91 (d, ^3J = 8.8 Hz, 4H, *H*-e), 3.82 (s, 6H, *H*-g), 2.96 (s, 4H, *H*-l) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 159.4 (*C*-f), 154.3 (*C*-j), 139.7 (*C*-b), 132.7 (*C*-c), 128.5 (*C*-k), 128.1 (*C*-d), 127.9 (*C*-a), 125.1 (*C*-h), 120.0 (*C*-i), 114.3 (*C*-e), 55.5 (*C*-g), 32.2 (*C*-l) ppm.
IR (ATR): $\tilde{\nu}$ = 2923 (w), 2851 (w), 2223 (w), 1887 (w), 1606 (m), 1579 (w), 1513 (m), 1478 (m), 1461 (m), 1451 (m), 1440 (m), 1307 (w), 1289 (w), 1242 (s), 1179 (s), 1110 (m), 1031 (w), 1018 (m), 956 (w), 925 (w), 894 (m), 834 (m), 821 (s), 802 (s), 723 (w) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{28}H_{24}N_2O_2]^+$ 420.18322; found 420.18361, 392.0 (100).
Mp: 211 °C**.**
R_f: 0.37 (cyclohexane/ethyl acetate 3/1), 0.45 (cyclohexane/DCM/ ethyl acetate 5/4/1).

(*Z*)-4,4'-(11,12-Dihydrodibenzo[*c*,*g*][1,2]diazocine-2,9-diyl)diphenol (**13**)



Stille cross-coupling reaction:

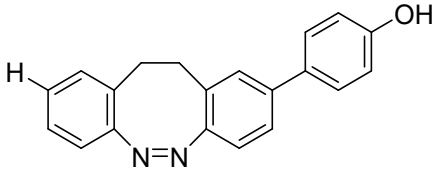
Compound **13** was synthesized according to the general procedure from 4-bromophenol (34.6 mg, 200 µmol) using pre-milled $Pd(OAc)_2$/XPhos (1:3 ratio, 16.5 mg, 10.0 µmol, 10 mol%). The reaction mixture was stirred for 3 d at 80 °C. The product **13** was obtained after purification via column chromatography on silica (eluent: DCM → DCM/MeOH 99/1) as a yellow solid (22.0 mg, 56.4 µmol, 56%).

Suzuki cross-coupling reaction:

Compound **13** was synthesized according to the general procedure from 4-bromophenol (34.6 mg, 200 µmol). No product was obtained.

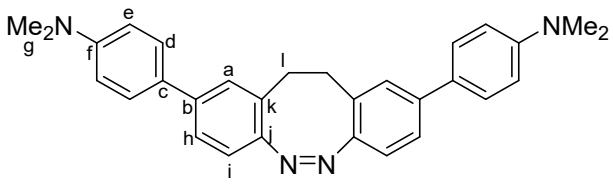
^{1}H NMR (600 MHz, DMSO-d_6) δ = 9.53 (s, 2H, *H*-g), 7.41 (d, ^3J = 8.7 Hz, 4H, *H*-d), 7.40 (dd, ^3J = 8.2 Hz, ^4J = 2.0 Hz, 2H, *H*-h), 7.34 (ad, ^4J = 2.0 Hz, 2H, *H*-a), 6.93 (d, ^3J = 8.2 Hz, 2H, *H*-i), 6.77 (d, ^3J = 8.7 Hz, 4H, *H*-e), 2.93 – 2.86 (m, 4H, *H*-l) ppm.
^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ = 157.3 (*C*-f), 153.6 (*C*-j), 138.8 (*C*-b), 129.6 (*C*-c), 128.4 (*C*-k), 127.6 (*C*-d), 127.1 (*C*-a), 124.2 (*C*-h), 119.5 (*C*-i), 115.7 (*C*-e), 31.2 (*C*-l) ppm.
IR (ATR): $\tilde{\nu}$ = 3352 (br), 2930 (w, br), 1610 (m), 1593 (m), 1516 (s), 1478 (m), 1457 (m), 1380 (m), 1244 (s), 1172 (m), 1106 (w), 1003 (w), 898 (m), 814 (s), 802 (s), 755 (s) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{26}H_{20}N_2O_2]^+$ 392.15193; found 392.15221, 364.0 (100).
Mp: 190 °C**.**
R_f: 0.07 (DCM).

Side Product of the Suzuki Cross-Coupling Reaction (Z)-4-(11,12-dihydrodibenzo-[*c,g*][1,2]diazocin-2-yl)phenol (**32**)



^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.37 (d, ^3J = 8.6 Hz, 1H), 7.33 (d, ^3J = 8.8 Hz, 2H), 7.15 (d, ^4J = 2.0 Hz, 1H), 7.05 – 6.96 (m, 2H), 6.91 – 6.87 (m, 1H), 6.87 – 6.83 (m, 2H), 6.73 (d, ^3J = 8.8 Hz, 2H), 4.87 (s, 1H), 3.12 – 2.92 (m, 2H), 2.91 – 2.72 (m, 2H) ppm.
MS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{20}H_{16}N_2O]^+$ 300.13; found 300 .1 (45), 272.1 (100).

(*Z*)-4,4'-(11,12-Dihydrodibenzo[*c*,*g*][1,2]diazocine-2,9-diyl)bis(*N*,*N*-dimethylaniline)-diazocine (**14**)



Stille cross-coupling reaction:

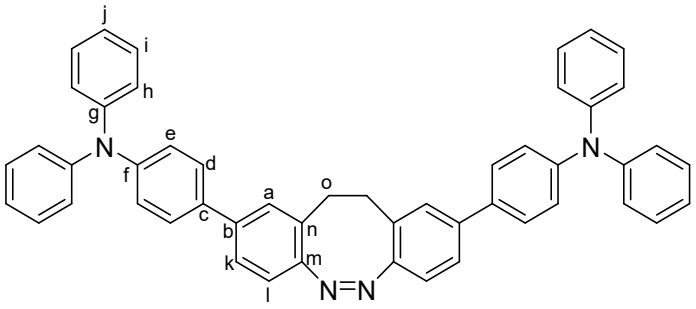
Compound **14** was synthesized according to the general procedure from 4-bromo-*N*,*N*-dimethylaniline (40.0 mg, 200 µmol). The product **14** was obtained after purification via column chromatography on silica (eluent: cyclohexane/ethyl acetate 3/1) as a yellow solid (40.6 mg, 90.9 µmol, 91%).

Suzuki cross-coupling reaction:

Compound **14** was synthesized according to the general procedure from 4-bromo-*N*,*N*-dimethylaniline (40.0 mg, 200 µmol). The product **14** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM/ethyl acetate 5/4/1) as a yellow solid (13.7 mg, 30.7 µmol, 31%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.40 (d, ^3J = 8.2 Hz, 4H, *H*-d), 7.34 (dd, ^3J = 8.2 Hz, ^4J = 1.9 Hz, 2H, *H*-h), 7.18 (ad, ^4J = 1.9 Hz, 2H, *H*-a), 6.93 (d, ^3J = 8.2 Hz, 2H, *H*-i), 6.73 (d, ^3J = 8.2 Hz, 4H, *H*-e), 3.08 – 2.79 (m, 16H, *H*-g, l) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 153.8 (*C*-j), 150.2 (*C*-f), 140.0 (*C*-b), 128.4 (*C*-k), 128.1 (*C*-c), 127.6 (*C*-d), 127.4 (*C*-a), 124.6 (*C*-h), 120.0 (*C*-i), 112.8 (*C*-e), 40.7 (*C*-l), 32.3 (*C*-g) ppm.
IR (ATR): $\tilde{\nu}$ = 2922 (w), 2852 (w), 1888 (w), 1606 (m), 1579 (w), 1513 (m), 1478 (m), 1462 (m), 1451 (m), 1440 (m), 1307 (w), 1242 (s), 1179 (m), 1110 (w), 1031 (m), 1018 (m), 987 (w), 956 (w), 895 (w), 835 (m), 825 (m), 802 (s) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{30}H_{30}N_4]^+$ 446.24650; found 446.24601, 446.1(100).
Mp: 268 °C**.**
R$_f$: 0.40 (cyclohexane/ethyl acetate 3/1), 0.52(cyclohexane/DCM/ethyl acetate 5/4/1).

(*Z*)-4,4'-(11,12-Dihydrodibenzo[*c*,*g*][1,2]diazocine-2,9-diyl)bis(*N,N*-diphenylaniline) (**15**)



Stille cross-coupling reaction:

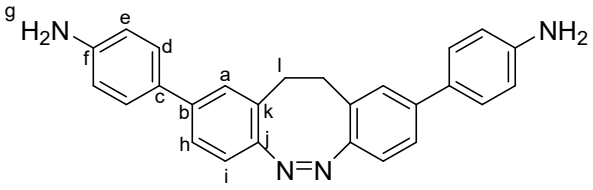
Compound **15** was synthesized according to the general procedure from 4-bromodiphenylamine (68.4 mg, 200 µmol). The product **15** was obtained after purification via column chromatography on silica (eluent: DCM) as a yellow solid (59.8 mg, 86.0 µmol, 86%).

Suzuki cross-coupling reaction:

Compound **15** was synthesized according to the general procedure from 4-bromodiphenylamine (68.4 mg, 200 µmol). The product **15** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM/ethyl acetate 5/4/1) as a yellow solid (50.4 mg, 72.4 µmol, 72%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.39 – 7.34 (m, 6H, *H*-d/k), 7.26 – 7.23 (m, 8H, *H*-i), 7.20 (ad, ^4J = 1.9 Hz, 2H, *H*-a), 7.11 – 7.06 (m, 12H, *H*-h/e), 7.02 (tt, ^3J = 7.4 Hz, ^4J = 1.2 Hz, 4H, *H*-j), 6.93 (d, ^3J = 8.2 Hz, 2H, *H*-l), 3.10 – 2.80 (m, 4H, *H*-o) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 154.5 (*C*-m), 147.7 (*C*-g), 147.5 (*C*-f), 139.5 (*C*-b), 134.0 (*C*-c), 129.4 (*C*-i), 128.6 (*C*-n), 127.8 (*C*-a), 127.7 (*C*-d), 125.0 (*C*-k), 124.5 (*C*-h), 124.0 (*C*-e), 123.1 (*C*-j), 119.8 (*C*-l), 32.2 (*C*-o) ppm.
IR (ATR): $\tilde{\nu}$ = 3033 (br, w), 1589 (s), 1513 (m), 1478 (s), 1325 (m), 1272 (s), 1176 (w), 1075 (w), 1028 (w), 897 (w), 819 (m), 804 (m), 752 (s) cm^{-1}.
HRMS (APCI) *m/z* (%): $[M+H]^+$ calcd for $[C_{50}H_{38}N_4 + H]^+$ 695.31692; found 695.31639, 134.0 (100).
Mp: 134 °C**.**
R_f: 0.48 (DCM), 0.62 (cyclohexane/DCM/ethyl acetate 5/4/1).

(*Z*)-4,4'-(11,12-Dihydrodibenzo[*c*,*g*][1,2]diazocine-2,9-diyl)dianiline (16)



Stille cross-coupling reaction:

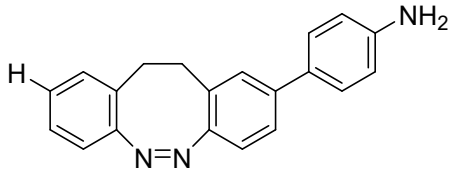
Compound **16** was synthesized according to the general procedure from 4-bromoaniline (34.4 mg, 200 µmol) using pre-milled $Pd(OAc)_2$/XPhos (1:3 ratio, 16.5 mg, 10.0 µmol, 10 mol%). The reaction mixture was stirred for 3 d at 80 °C. The product **16** was obtained after purification via column chromatography on silica (eluent: DCM → DCM/MeOH 99/1) as a yellow solid (18.3 mg, 46.9 µmol, 47%).

Suzuki cross-coupling reaction:

Compound **16** was synthesized according to the general procedure from 4-bromoaniline (34.4 mg, 200 µmol). No product was obtained.

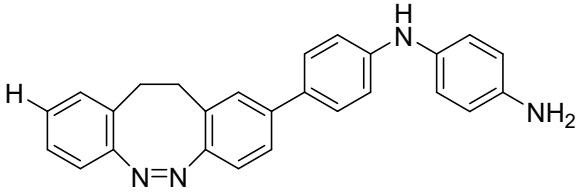
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.33 – 7. 29 (m, 6H, *H*-d, h), 7.16 (ad, ^4J = 1.9 Hz, 2H, *H*-a), 6.92 (d, ^3J = 8.1 Hz, 2H, *H*-i), 6.69 (d, ^3J = 8.1 Hz, 4H, *H*-e), 3.70 (s, br, 4H, *H*-g), 3.09 – 2.76 (m, 4H, *H*- l) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 154.0 (*C*-j), 146.1 (*C*-f), 140.0 (*C*-b), 130.5 (*C*-c), 128.4 (*C*-k), 127.9 (*C*-d), 127.5 (*C*-a), 124.7 (*C*-h), 119.9 (*C*-i), 115.5 (*C*-e), 32.2 (*C*-l) ppm.
IR (ATR): $\tilde{\nu}$ = 3348 (br, m), 2926 (br, w), 1601 (s), 1517 (s), 1477 (s), 1432 (w), 1378 (m), 1278 (s), 1182 (m), 1129 (m), 895 (m), 819 (s), 804 (s) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{26}H_{22}N_4]^+$ 390.18390; found 390.18436, 362.1 (100).
Mp: 144 °C**.**
R_f: 0.10 (DCM).

Side Product of the Suzuki Cross-Coupling Reaction (*Z*)-4-(11,12-dihydrodibenzo-[*c,g*][1,2]diazocin-2-yl)aniline (**33**)



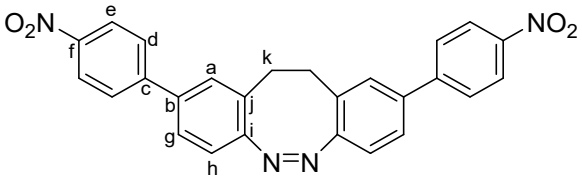
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.30 (m, 3H), 7.14 (d, ^4J = 2.2 Hz, 2H), 7.06 – 6.98 (m, 2H), 6.90 – 6.85 (m, 2H), 6.70 (d, ^3J = 8.4 Hz, 2H), 3.71 (s, 2H), 3.10 – 2.95 (m, 2H), 2.85 – 2.72 (m, 2H) ppm.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{20}H_{17}N_3]^+$ 299.14159; found 299.14170, 271.2 (100).

Side Product of the Suzuki Cross-Coupling Reaction (*Z*)-*N*1-(4-(11,12-dihydrodi-benzo[*c,g*][1,2]diazocin-2-yl)phenyl)benzene-1,4-diamine (**34**)



^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.33 (d, ^3J = 8.6 Hz, 2H), 7.31 (dd, ^3J = 8.3 Hz, ^4J = 1.9 Hz, 1H), 7.17 – 7.12 (m, 2H), 7.05 – 6.95 (m, 4H), 6.90 – 6.83 (m, 4H), 6.68 (d, ^3J = 8.5 Hz, 2H), 5.47 (s, 1H), 3.56 (s, 2H), 3.16 – 2.95 (m, 2H), 2.87 – 2.73 (m, 2H) ppm.
MS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{26}H_{22}N_4]^+$ 390.18; found 390.2 (40), 107.0 (100).

(*Z*)-2,9-Bis(4-nitrophenyl)-11,12-dihydrodibenzo[*c,g*][1,2]diazocine (**17**)



Stille cross-coupling reaction:

Compound **17** was synthesized according to the general procedure from 1-bromo-4-nitrobenzene (40.4 mg, 200 µmol). The product **17** was obtained after purification via column chromatography on silica (eluent: cyclohexane/ethyl acetate 3/1) as a yellow solid (40.1 mg, 89.0 µmol, 89%).

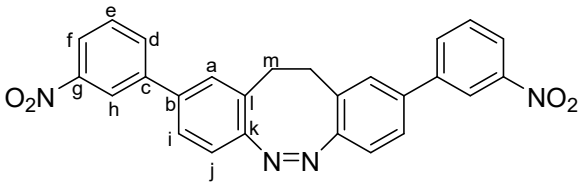
Suzuki cross-coupling reaction:

Compound **17** was synthesized according to the general procedure from 1-bromo-4-nitrobenzene (40.4 mg, 200 µmol). The product **17** was obtained after purification via column chromatography on silica (eluent cyclohexane/DCM/ethyl acetate 5/4/1) as a yellow solid (36.1 mg, 80.1 µmol, 80%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.24 (d, ^3J = 8.7 Hz, 4H, *H*-e), 7.64 (d, ^3J = 8.7 Hz, 4H, *H*-d), 7.45 (dd, ^3J = 8.2 Hz, ^4J = 1.9 Hz, 2H, *H*-g), 7.29 (ad, ^4J = 1.9 Hz, 2H, *H*-a), 7.04 (d, ^3J = 8.2 Hz, 2H, *H*-h), 3.20 – 2.83 (m, 4H, *H*-k) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 155.9 (*C*-i), 147.3 (*C*-f), 146.4 (*C*-c), 137.8 (*C*-b), 128.9 (*C*-a), 128.9 (*C*-j), 127.7 (*C*-d), 126.2 (*C*-g), 124.3 (*C*-e), 120.2 (*C*-h), 32.0 (*C*-k) ppm.

IR (ATR): $\tilde{\nu}$ = 2930 (w), 1592 (m), 1509 (s), 1339 (s), 1165 (w), 1110 (m), 1011 (w), 956 (w), 909 (w), 862 (m), 850 (s), 836 (m), 830 (m), 809 (m), 752 (s), 741 (m), 724 (w), 689 (m) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{26}H_{18}N_4O_4]^+$ 450.13226; found 450.13225, 44.0 (100).
Mp: 225 °C**.**
R_f: 0.29 (cyclohexane/ethyl acetate 3/1), 0.44 (cyclohexane/DCM/ethyl acetate 5/4/1).

(*Z*)-2,9-Bis(3-nitrophenyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**18**)



Stille cross-coupling reaction:

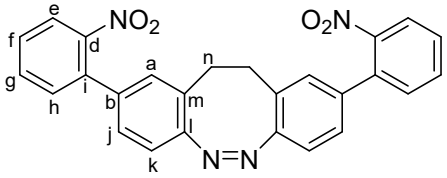
Compound **18** was synthesized according to the general procedure from 1-bromo-3-nitrobenzene (40.4 mg, 200 µmol). The product **18** was obtained after purification via column chromatography on silica (eluent: DCM) as a yellow solid (34.5 mg, 85.3 µmol, 85%).

Suzuki cross-coupling reaction:

Compound **18** was synthesized according to the general procedure from 1-bromo-3-nitrobenzene (40.4 mg, 200 µmol). The product **18** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM/ethyl acetate 5/4/1) as a yellow solid (39.6 mg, 88.1 µmol, 88%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (dd, ^4J = 2.3 Hz, 2.0 Hz, 2H, *H*-h), 8.16 (ddd, ^3J = 8.0 Hz, ^4J = 2.3 Hz, ^4J = 1.0 Hz, 2H, *H*-f), 7.83 (ddd, ^3J = 7.7 Hz, ^4J = 2.0 Hz, ^4J = 1.0 Hz, 2H, *H*-d), 7.56 (dd, ^3J = 8.0 Hz, ^3J = 7.7 Hz, 2H, *H*-e), 7.44 (dd, ^3J = 8.2, ^4J = 2.0 Hz, 2H, *H*-i), 7.30 (d, ^4J = 2.0 Hz, 2H, *H*-a), 7.03 (d, ^3J = 8.2 Hz, 2H, *H*-j), 3.23 – 2.84 (m, 4H, m) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 155.7 (*C*-k), 148.8 (*C*-g), 141.7 (*C*-b), 137.7 (*C*-c), 133.0 (*C*-d), 129.9 (*C*-e), 129.0 (*C*-l), 128.7 (*C*-a), 125.9 (*C*-i), 122.4 (*C*-f), 121.9 (*C*-h), 120.1 (*C*-j), 32.0 (*C*-m) ppm.
IR (ATR): $\tilde{\nu}$ = 3078 (w), 2924 (br, w), 1523 (s), 1470 (w), 1345 (s), 1103 (w), 1084 (w), 892 (m), 842 (m), 801 (m), 736 (s) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{26}H_{18}N_4O_4]^+$ 450.13226; found 450.13181, 422.0 (100).
Mp: 150 °C**.**
R_f: 0.36 (DCM), 0.47 (cyclohexane/DCM/ethyl acetate 5/4/1).

(*Z*)-2,9-Bis(2-nitrophenyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**19**)



Stille cross-coupling reaction:

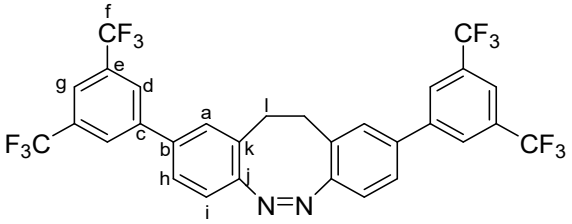
Compound **19** was synthesized according to the general procedure from 1-bromo-2-nitrobenzene (40.4 mg, 200 µmol). The product **19** was obtained after purification via column chromatography on silica (eluent: DCM) as a yellow solid (39.7 mg, 88.2 µmol, 88%).

Suzuki cross-coupling reaction:

Compound **19** was synthesized according to the general procedure from 1-bromo-2-nitrobenzene (40.4 mg, 200 µmol). The product **19** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM/ethyl acetate 5/4/1) as a yellow solid (31.2 mg, 69.2 µmol, 69%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.82 (dd, ^3J = 8.1 Hz, ^4J = 1.3 Hz, 2H, *H*-e), 7.57 (ddd, ^3J = 7.7 Hz, ^3J = 7.5 Hz, ^4J = 1.3 Hz, 2H, *H*-g), 7.45 (ddd, ^3J = 8.1 Hz, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 2H, *H*-f), 7.38 (dd, ^{3}J = 7.7 Hz, ^4J = 1.5 Hz, 2H, *H*-h), 7.10 (dd, ^3J = 8.0 Hz, ^4J = 1.9 Hz, 2H, *H*-j), 6.93 (d, ^4J = 1.9 Hz, 2H, *H*-a), 6.88 (d, ^3J = 8.0 Hz, 2H, *H*-k), 3.11 – 2.71 (m, 4H, *H*-n) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 155.6 (*C*-l), 149.2 (*C*-d), 136.5 (*C*-b), 135.6 (*C*-i), 132.5 (*C*-g), 132.2 (*C*-h), 129.3 (*C*-a), 128.9 (*C*-m), 128.5 (*C*-f), 126.6 (*C*-j), 124.2 (*C*-e), 119.0 (*C*-k), 31.6 (*C*-n)
IR (ATR): $\tilde{\nu}$ = 2922 (br, w), 1603 (w), 1519 (s), 1468 (m), 1345 (m), 1288 (w), 1085 (m), 899 (m), 781 (s), 750 (s), 732 (m) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{26}H_{18}N_4O_4]^+$ 450.13226; found 450.13003, 326.2 (100).
Mp: 151 °C**.**
R_f: 0.34 (DCM), 0.50 (cyclohexane/DCM/ethyl acetate 5/4/1).

(*Z*)-2,9-Bis(3,5-bis(trifluoromethyl)phenyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (20)



Stille cross-coupling reaction:

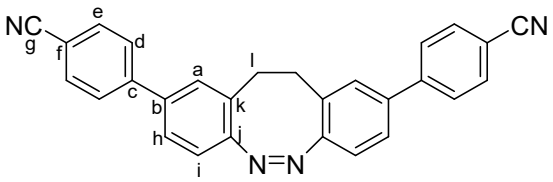
Compound **20** was synthesized according to the general procedure from 3,5-bis(trifluoromethyl)-brombenzene (58.6 mg, 200 µmol). The product **20** was obtained after purification via crystallization from DCM/MeOH (*v/v* 1/1) at -21 °C as a yellow solid (56.7 mg, 89.7 µmol, 90%).

Suzuki cross-coupling reaction:

Compound **20** was synthesized according to the general procedure from 3,5-bis(trifluoromethyl)-bromobenzene (58.6 mg, 200 µmol). The product **20** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM/ethyl acetate 5/4/1) as a yellow solid (53.1 mg, 84.0 µmol, 84%).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.92 – 7.90 (m, 4H, *H*-d), 7.83 – 7.79(m, 2H, *H*-g), 7.44 (dd, ^3J = 8.1 Hz, ^4J = 2.0 Hz, 2H, *H*-h), 7.28 (d, ^4J = 2.0 Hz, 2H, *H*-a), 7.05 (d, ^3J = 8.1 Hz, 2H, *H*-i), 3.23 – 2.90 (m, 4H, *H*-l) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ = 155.9 (*C*-j), 142.1 (*C*-c), 137.3 (*C*-b), 132.4 (q, *J* = 33.4 Hz, *C*-e), 129.1 (*C*-k), 128.7 (*C*-a), 127.1 (d, *J* = 3.8 Hz, *C*-d), 126.0 (*C*-h), 124.5 (*C*-f), 122.3 (*C*-f), 121.3 (m, *C*-g) 120.3 (*C*-i), 31.9 (*C*-l) ppm.
^{19}F NMR (471 MHz, $CDCl_3$) δ = -63.4 ppm.
IR (ATR): $\tilde{\nu}$ = 2929 (w), 1465 (w), 1377 (s), 1278 (s), 1158 (m), 1128 (s), 1116 (s), 1056 (m), 893 (m), 882 (m), 845 (m), 825 (m), 805 (m), 776 (w), 708 (m9, 701 (m) cm^{-1}.
HRMS (APCI) *m/z* (%): $[M+H]^+$ calcd for $[C_{30}H_{16}F_{12}N_2 + H]^+$ 633.11946; found 633.11894, 134.0 (100).
Mp: 216 °C**.**
R_f: 0.35 (cyclohexane/ethyl acetate 9/1), 0.65 (cyclohexane/DCM/ethyl acetate 5/4/1).

(*Z*)-4,4'-(11,12-Dihydrodibenzo[*c*,*g*][1,2]diazocine-2,9-diyl)dibenzonitrile (**21**)



Stille cross-coupling reaction:

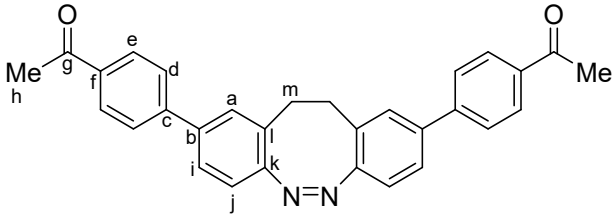
Compound **21** was synthesized according to the general procedure from 4-bromobenzonitrile (36.4 mg, 200 µmol) with a reaction time of 4 h. The product **21** was obtained after purification via column chromatography on silica (eluent: cyclohexane/ethyl acetate 3/1) as a yellow solid (36.6 mg, 89.2 µmol, 89%).

Suzuki cross-coupling reaction:

Compound **21** was synthesized according to the general procedure from 4-bromotoluene (34.2 mg, 200 µmol). The product **21** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM/ethyl acetate 5/4/1) as a yellow solid (29.6 mg, 72.2 µmol, 72%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.67 (d, ^3J = 8.7 Hz, 4H, *H*-e), 7.58 (d, ^3J = 8.7 Hz, 4H, *H*-d), 7.40 (dd, ^3J = 8.2 Hz, ^4J = 1.9 Hz, 2H, *H*-h), 7.24 (ad, ^4J = 1.9 Hz, 2H, *H*-a), 7.01 (d, ^3J = 8.2 Hz, 2H, *H*-i), 3.41 – 2.62 (m, 4H, *H*-l) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 155.7 (*C*-j), 144.4 (*C*-c), 138.2 (*C*-b), 132.7 (*C*-e), 128.9 (*C*-k), 128.7 (*C*-a), 127.6 (*C*-d), 125.9 (*C*-h), 120.1 (*C*-i), 118.9 (*C*-g), 111.4 (*C*-f), 32.0 (*C*-l) ppm.
IR (ATR): $\tilde{\nu}$ = 2894 (w), 1682 (s), 1675 (s), 1601 (m), 1555 (w), 1519 (w), 1478 (w), 1434 (w), 1418 (w), 1391 (w), 1357 (m), 1317 (w), 1272 (m), 1258 (s), 1199 (m), 1199 (w), 1012 (w), 961.3 (m), 925 (w), 900 (m), 893 (m), 851 (w), 836 (m), 817 (s), 800 (s), 754 (w), 726 (w), 691 (w), 659 (w) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{28}H_{18}N_4]^+$ 410.15260; found 410.15298, 382.0 (100).
Mp: 238 °C**.**
R_f: 0.25 (cyclohexane/ethyl acetate 3/1), 0.31(cyclohexane/DCM/ethyl acetate 5/4/1).

(*Z*)-1,1'-((11,12-Dihydrodibenzo[*c*,*g*][1,2]diazocine-2,9-diyl)bis(4,1-phenylene))bis-(ethan-1-one) (**22**)



Stille cross-coupling reaction:

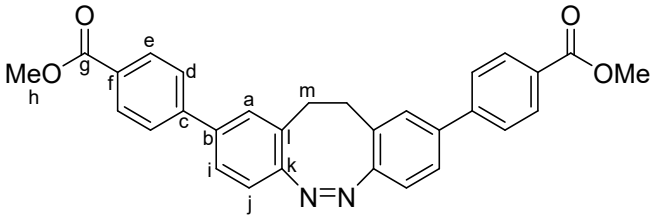
Compound **22** was synthesized according to the general procedure from 4-bromoacetophenone (39.8 mg, 200 µmol). The product **22** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM 1/1) as a yellow solid (36.5 mg, 82.1 µmol, 82%).

Suzuki cross-coupling reaction:

Compound **22** was synthesized according to the general procedure from 4-bromoacetophenone (39.8 mg, 200 µmol). The product **22** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM/ethyl acetate 5/4/1 → 2/2/1) as a yellow solid (26.2 mg, 58.9 µmol, 59%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.97 (d, ^3J = 8.4 Hz, 4H, *H*-e), 7.59 (d, ^3J = 8.4 Hz, 4H, *H*-d), 7.44 (dd, ^3J = 8.2 Hz, ^4J = 1.9 Hz, 2H, *H*-i), 7.29 (ad, ^4J = 1.9 Hz, 2H, *H*-a), 7.01 (d, ^3J = 8.2 Hz, 2H, *H*-j), 3.22 – 2.77 (m, 4H, *H*-m), 2.61 (s, 6H, *H*-h) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 197.8 (*C*-g), 155.5 (*C*-k), 144.6 (*C*-c), 138.9 (*C*-b), 136.2 (*C*-f), 129.0 (*C*-e), 128.7 (*C*-l), 128.7 (*C*-a), 127.1 (*C*-d), 125.9 (*C*-i), 120.0 (*C*-j), 32.1 (*C*-m), 26.8 (*C*-h) ppm.
IR (ATR): $\tilde{\nu}$ = 2894 (w), 1682 (s), 1674 (s), 1601 (m), 1556 (w), 1520 (w), 1476 (w), 1460 (w), 1434 (w), 1418 (w), 1390 (w), 1356 (m), 1272 (m), 1258 (s), 1199 (m), 1166 (w), 1120 (w), 1101 (w), 1079 (w), 1023 (w), 1012 (w), 962 (m), 900 (m), 893 (m), 851 (w), 836 (m), 817 (s), 799 (s), 754 (m), 726 (w), 691 (w), 659 (w) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{30}H_{24}N_2O_2]^+$ 444.18323; found 444.18275, 43.0 (100).
Mp: 189 °C**.**
R_f: 0.45 (cyclohexane/ethyl acetate 1/1), 0.29 (cyclohexane/DCM/ethyl acetate 5/4/1)

Dimethyl 4,4'-(11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine-2,9-diyl)(*Z*)-dibenzoate (**23**)



Stille cross-coupling reaction:

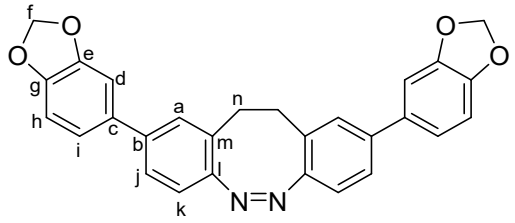
Compound **23** was synthesized according to the general procedure from methyl-4-bromobenzoate (43.0 mg, 200 µmol). The product **23** was obtained after purification via crystallization from DCM/*n*-hexane (*v/v* 1/2) at -21 °C as a yellow solid (38.3 mg, 80.2 µmol, 80%).

Suzuki cross-coupling reaction:

Compound **23** was synthesized according to the general procedure from methyl-4-bromobenzoate (43.0 mg, 200 µmol). The product **23** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM/ethyl acetate 5/4/1) as a yellow solid (27.7 mg, 58.2 µmol, 58%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.04 (d, ^3J = 8.4 Hz, 4H, *H*-e), 7.56 (d, ^3J = 8.4 Hz, 4H, *H*-d), 7.43 (dd, ^3J = 8.2 Hz, ^4J = 1.9 Hz, 2H, *H*-i), 7.28 (ad, ^4J = 1.9 Hz, 2H, *H*-a), 7.00 (d, ^3J = 8.2 Hz, 2H, *H*-j), 3.91 (s, 6H, *H*-h), 3.12 – 2.88 (m, 4H, *H*-m) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 167.0 (*C*-g), 155.4 (*C*-k), 144.4 (*C*-c), 139.0 (*C*-b), 130.2 (*C*-e), 129.2 (*C*-f), 128.7 (*C*-a), 126.9 (*C*-d), 125.9 (*C*-i), 119.9 (*C*-j), 52.3 (*C*-h), 32.1 (*C*-m) ppm.
IR (ATR): $\tilde{\nu}$ = 2944 (br, w), 1711 (s), 1607 (w), 1522 (m), 1430 (m), 1345 (m), 1276 (s), 1183 (m), 1103 (s), 1015 (m), 962 (w), 894 (m), 802 (m), 766 (s), 740 (m) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{30}H_{24}N_2O_4]^+$ 476.17306; found 476.17340, 58.9 (100).
Mp: 233 °C**.**
R_f: 0.37 (cyclohexane/ethyl acetate 3/1), 0.48 (cyclohexane/DCM/ethyl acetate 5/4/1)

(*Z*)-2,9-Bis(benzo[*d*][1,3]dioxol-5-yl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**24**)



Stille cross-coupling reaction:

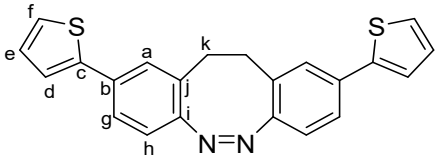
Compound **24** was synthesized according to the general procedure from 5-bromobenzo[d][1,3]dioxole (40.2 mg, 200 µmol). The product **24** was obtained after purification via column chromatography on silica (eluent: DCM) as a yellow solid (31.5 mg, 70.3 µmol, 70%).

Suzuki cross-coupling reaction:

Compound **24** was synthesized according to the general procedure from 5-bromobenzo[d][1,3]dioxole (40.2 mg, 200 µmol). The product **24** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM/ethyl acetate 5/4/1) as a yellow solid (33.7 mg, 75.1 µmol, 75%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.30 (dd, ^3J = 8.1 Hz, ^4J = 1.9 Hz, 2H, *H*-j), 7.14 (ad, ^4J = 1.9 Hz, 2H, *H*-a), 6.98 – 6.96 (m, 4H, *H*-d/h), 6.93 (d, ^3J = 8.1 Hz, 2H, *H*-k), 6.82 (d, ^3J = 7.7 Hz, ^4J = 0.8 Hz, 2H, *H*-i), 5.96 (s, 4H, *H*-f), 3.12 – 2.78 (m, 4H, *H*-nl) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 154.5 (*C*-l), 148.3 (*C*-g), 147.4 (*C*-e), 139.8 (*C*-b), 134.5 (*C*-c), 128.5 (*C*-m), 128.1 (*C*-a), 125.3 (*C*-j), 120.6 (*C*-d), 119.9 (*C*-k), 108.7 (*C*-i), 107.6 (*C*-h), 101.3 (*C*-f), 32.1 (*C*-n) ppm.
IR (ATR): $\tilde{\nu}$ = 2987 (br, w), 1600 (w), 1504 (m), 1472 (s), 1436 (m), 1333 (w), 1256 (w), 1228 (s), 1102 (w), 1032 (s), 931 (s), 907 (m), 856 (m), 838 (m), 796 (s) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{28}H_{20}N_2O_4]^+$ 448.14176; found 448.14155, 420.0 (100).
Mp: 236 °C**.**
R$_f$: 0.24 (DCM), 0.44 (cyclohexane/DCM/ethyl acetate 5/4/1)

(*Z*)-2,9-Di(thiophen-2-yl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**25**)



Stille cross-coupling reaction:

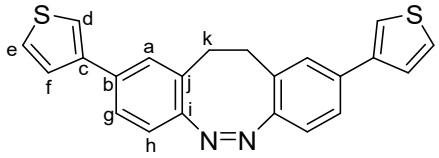
Compound **25** was synthesized according to the general procedure from 3-bromothiophene (32.6 mg, 200 µmol). The product **25** was obtained after purification via crystallization from MeOH at -21 °C as a yellow solid (33.7 mg, 90.3 µmol, 90%).

Suzuki cross-coupling reaction:

Compound **25** was synthesized according to the general procedure from 3-bromothiophene (32.6 mg, 200 µmol). The product **25** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM/ethyl acetate 5/4/1) as a yellow solid (24.0 mg, 64.3 µmol, 64%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.40 (dd, ^3J = 8.2 Hz, ^4J = 1.9 Hz, 2H, *H*-g), 7.25 (ad, ^4J = 1.9 Hz, 2H, *H*-a), 7.24 – 7.21 (m, 4H, *H*-d, e), 7.04 – 7.00 (m, 2H, *H*-f), 6.90 (d, ^3J = 8.2 Hz, 2H, *H*-h), 3.08 – 2.80 (m, 4H, *H*-k) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 154.8 (*C*-i), 143.3 (*C*-c), 133.5 (*C*-b), 128.7 (*C*-j), 128.2 (*C*-f), 127.1 (*C*-a), 125.1 (*C*-e), 124.4 (*C*-g), 123.4 (*C*-d), 119.9 (*C*-h), 31.9 (*C*-k) ppm.
IR (ATR): $\tilde{\nu}$ = 3094 (w, br), 2919 (w, br), 1601 (w), 1507 (w), 1476 (m), 1460 (m), 1425 (w), 1341 (w), 1256 (m), 1218 (w), 1161 (w), 1076 (m), 1049 (m), 894 (m), 854 (m), 826 (s), 802 (s), 701 (s) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{22}H_{16}N_2S_2]^+$ 372.07494; found 372.07541, 371.9.0 (100).
Mp: 218 °C**.**
R_f: 0.26 (cyclohexane/DCM 2/1), 0.55 (cyclohexane/DCM/ethyl acetate 5/4/1).

(*Z*)-2,9-Di(thiophen-3-yl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**26**)



Stille cross-coupling reaction:

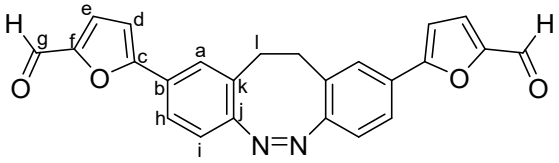
Compound **26** was synthesized according to the general procedure from 3-bromothiophene (32.6 mg, 200 µmol). The product **26** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM 1/2) as a yellow solid (34.9 mg, 93.6 µmol, 94%).

Suzuki cross-coupling reaction:

Compound **26** was synthesized according to the general procedure from 3-bromothiophene (32.6 mg, 200 µmol). The product **26** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM/ethyl acetate 5/4/1)as a yellow solid (24.7 mg, 66.2 µmol, 70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.39 – 7.35 (m, 4H, *H*-d,g), 7.33 (dd, ^3J = 5.0, ^4J = 3.0 Hz, 2H, *H*-e), 7.28 (dd, ^3J = 5.0, ^4J =1.4 Hz, 2H, *H*-f), 7.23 (d, ^4J = 1.9 Hz, 2H, *H*-a), 6.91 (d, ^3J = 8.1 Hz, 2H, *H*-h), 3.11-2.72(m, 4H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ = 154.5 (*C*-i), 141.2 (*C*-c), 134.7 (*C*-b), 128.5 (*C*-j), 127.5 (*C*-a), 126.3 (*C*-e), 126.0 (*C*-f), 124.8 (*C*-g), 120.4(*C*-d), 119.7 (*C*-h), 31.9 (*C*-k) ppm.
IR (ATR): $\tilde{\nu}$ = 3093 (w, br), 2954 (w, br), 1601 (w), 1504 (w), 1477 (m), 1462 (m), 1426 (w), 1204 (m), 1163 (w), 1086 (m), 1041 (w), 892 (s), 872 (m), 845 (s), 778 (s), 733 (m) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{22}H_{16}N_2S_2]^+$ 372.07494; found 372.07508, 343.9.0 (100).
Mp: 218 °C**.**
R_f: 0.26 (cyclohexane/DCM 2/1), 0.55 (cyclohexane/DCM/ethyl acetate 5/4/1).

(*Z*)-5,5'-(11,12-Dihydrodibenzo[*c*,*g*][1,2]diazocine-2,9-diyl)bis(furan-2-carbaldehyde) (**27**)



Stille cross-coupling reaction:

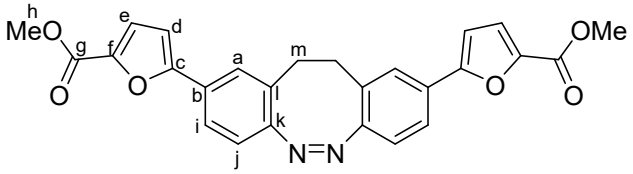
Compound **27** was synthesized according to the general procedure from 5-bromofuran-2-carbaldehyde (35.0 mg, 200 µmol). The product **27** was obtained after purification via column chromatography on silica (eluent: DCM → DCM/MeOH 95/5) as a yellow solid (36.1 mg, 91.1 µmol, 91%).

Suzuki cross-coupling reaction:

Compound **27** was synthesized according to the general procedure from 5-bromofuran-2-carbaldehyde (35.0 mg, 200 µmol). The product **27** was obtained after purification via column chromatography on silica (eluent: DCM → DCM/MeOH 95/5) as a yellow solid (15.5 mg, 39.0 µmol, 39%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.59 (s, 2H, *H*-g), 7.57 (dd, ^3J = 8.2 Hz, ^4J = 1.8 Hz, 2H, *H*-h), 7.50 (ad, ^4J = 1.8 Hz, 2H, *H*-a), 7.25 (d, ^3J = 3.7 Hz, 2H, *H*-e), 6.93 (d, ^3J = 8.2 Hz, 2H, *H*-i), 6.75 (d, ^3J = 3.7 Hz, 2H, *H*-d), 3.08 – 2.88 (m, 4H, *H*-l) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 177.3 (*C*-g), 158.4 (*C*-c), 156.5 (*C*-j), 152.2 (*C*-f), 141.0 (*C*-e), 129.1 (*C*-b), 128.2 (*C*-k), 126.8 (*C*-a), 124.2 (*C*-h), 119.6 (*C*-i), 108.1 (*C*-d), 31.6 (*C*-l) ppm.
IR (ATR): $\tilde{\nu}$ = 3111 (w, br), 2926 (w, br), 1634 (s), 1515 (s), 1463 (s), 1408 (m), 1385 (w), 1255 (m), 1026 (s), 966 (m), 898 (m), 795 (s), 766 (s), 754 (s) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{24}H_{16}N_2O_4]^+$ 396.11046; found 396.11059, 44.0 (100).
Mp: 125 °C**.**
R_f: 0.36 (DCM/MeOH 95/5).

Dimethyl 5,5'-(11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine-2,9-diyl)(*Z*)-bis(furan-2-carboxylate) (**28**)



Stille cross-coupling reaction:

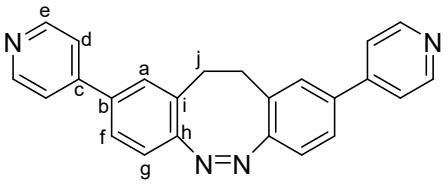
Compound **28** was synthesized according to the general procedure from methyl 5-bromofuran-2-carboxylate (41.0 mg, 200 µmol). The product **28** was obtained after purification via column chromatography on silica (eluent: DCM → DCM/MeOH 95/5) as a yellow solid (36.4 mg, 79.8 µmol, 80%).

Suzuki cross-coupling reaction:

Compound **28** was synthesized according to the general procedure from methyl 5-bromofuran-2-carboxylate (41.0 mg, 200 µmol). The product **28** was obtained after purification via column chromatography on silica (eluent: DCM → DCM/MeOH 95/5) as a yellow solid (26.1 mg, 57.2 µmol, 57%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.52 (dd, ^3J = 8.2 Hz, ^4J = 1.8 Hz, 2H, *H*-i), 7.45 (ad, ^4J = 1.8 Hz, 2H, *H*-a), 7.18 (d, ^3J = 3.6 Hz, 2H, *H*-e), 6.90 (d, ^3J = 8.2 Hz, 2H, *H*-j), 6.64 (d, ^3J = 3.6 Hz, 2H, *H*-d), 3.89 (s, 6H, *H*-h), 3.05 – 2.89 (m, 4H, *H*-m) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 159.2 (*C*-g), 156.6 (*C*-f), 156.0 (*C*-k), 143.8 (*C*-c), 129.0 (*C*-b), 128.6 (*C*-l), 126.2 (*C*-a), 123.6 (*C*-i), 120.1 (*C*-e), 119.6 (*C*-j), 107.3 (*C*-d), 52.1 (*C*-h), 31.6 (*C*-m) ppm.
IR (ATR): $\tilde{\nu}$ = 2948 (w, br), 1708 (s), 1587 (w), 1515 (m), 1465 (m), 1434 (m), 1408 (w), 1364 (w), 1297 (s), 1216 (m), 1190 (m), 1135 (s), 1024 (m), 987 (m), 925 (w), 899 (m), 795 (s), 757 (s) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{26}H_{20}N_2O_6]^+$ 456.13159; found 456.13126, 44.0 (100).
Mp: 115 °C**.**
R_f: 0.43 (DCM/MeOH 95/5).

(*Z*)-2,9-Di(pyridin-4-yl)-11,12-dihydrodibenzo*[c,g]*[1,2]diazocine (**29**)



Stille cross-coupling reaction:

Under inert conditions, the di-stannylated diazocine **3** (53.4 mg, 100 µmol, 1.00 equiv), 4-bromopyridine[7] (31.6 mg, 200 µmol, 2.00 equiv), pre-milled $Pd(OAc)_2$/XPhos (1:3 ration, 6.62 mg, 4.00 µmol, 4 mol%) and CsF (30.4 mg, 200 µmol, 2.00 equiv) were dissolved in dry 1,4-dioxane (2 mL) in a pressure reaction vial. The mixture was stirred at 80 °C for 4 d. After cooling to 23 °C, the reaction mixture was filtered through Celite® and the solvent was removed under reduced pressure. The product **29** was obtained after purification via column chromatography on silica (eluent: DCM → DCM/MeOH 95/5) as a yellow solid (35.0 mg, 89.7 µmol, 90%).

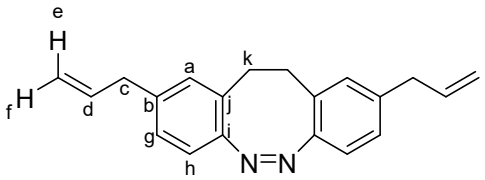
Suzuki cross-coupling reaction:

Under inert conditions, the di-borylated diazocine **5** (46.0 mg, 100 µmol, 1.00 equiv), $Pd(OAc)_2$ (1.12 mg, 5 µmol, 5 mol%), XPhos (4.77 mg, 10.0 µmol, 10 mol%), KOH aq (2 M, 1 mL) and 4-bromopyridine (31.6 mg, 200 µmol, 2.00 equiv)) were dissolved in THF (4 mL) and sealed in a pressure reaction vial. The mixture was stirred 90 °C for 18 h. After cooling to 23 °C, the reaction mixture was filtered through Celite® and the solvent was removed under reduced pressure. The product **29** was obtained after purification via column chromatography on silica (eluent: DCM → DCM/MeOH 95/5) as a yellow solid (18.6 mg, 50.1 µmol, 50%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.60 (dd, ^3J = 4.5 Hz, ^4J = 1.6 Hz, 4H, *H*-d), 7.45 (dd, ^3J = 8.2 Hz, ^4J = 1.9 Hz, 2H, *H*-f), 7.40 (dd, ^3J = 4.5 Hz, ^4J = 1.6 Hz, 4H, *H*-e), 7.29 (ad, ^4J = 1.9 Hz, 2H, *H*-a), 7.01 (d, ^3J = 8.2 Hz, 2H, *H*-g), 3.17 – 2.87 (m, 4H, *H*-j) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 156.0 (*C*-h), 150.4 (*C*-d), 147.1 (*C*-b), 137.2 (*C*-c), 128.9 (*C*-i), 128.5 (*C*-a), 125.7 (*C*-f), 121.5 (*C*- e), 120.0 (*C*-g), 32.0 (*C*-j) ppm.
IR (ATR): $\tilde{\nu}$ = 3027 (w), 2928 (w, br), 1595 (s), 1542 (w), 1475 (m), 1417 (m), 1395 (m), 1329 (w), 1221 (w), 1171 (w), 1069 (w), 993 (m), 901 (m), 832 (m), 814 (s), 799 (s) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{24}H_{18}N_4]^+$ 362.15260; found 362.15266, 334.1 (100).
Mp: 112 °C**.**
R_f: 0.16 (DCM/MeOH 95/5).

[7] Freshly prepared from 4-bromopyridine hydrochloride.

(*Z*)-2,9-Diallyl-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**30**)



Stille cross-coupling reaction:

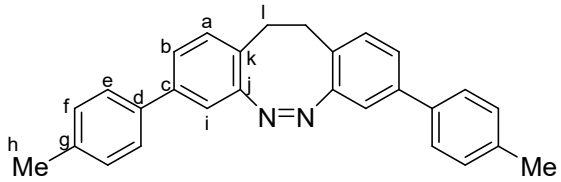
Compound **30** was synthesized according to the general procedure from 3-bromoprop-1-ene (24.2mg, 200 µmol). The product **30** was obtained after purification via column chromatography on silica (eluent: DCM) as a yellow oil (16.4 mg, 56.9 µmol, 57%).

Suzuki cross-coupling reaction:

Compound **30** was synthesized according to the general procedure from 3-bromoprop-1-ene (24.2 mg, 200 µmol). The product **30** was obtained after purification via column chromatography on silica (eluent: cyclohexane/DCM 3/2) as a yellow solid (18.1 mg, 62.9 µmol, 63%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 6.95 (dd, ^3J = 8.0 Hz, ^4J = 1.9 Hz, 2H, *H*-g), 6.80 (d, ^4J = 1.9 Hz, 2H, *H*-a), 6.78 (d, ^3J = 8.0 Hz, 2H, *H*-h), 5.87 (ddt, ^3J = 17.0 Hz, ^3J = 10.0 Hz, ^3J = 6.6 Hz, 2H, *H*-d), 5.03 (dq, ^3J = 10.0 Hz, ^2J = 1.5 Hz, 2H, *H*-f), 4.97 (dq, ^3J = 17.0 Hz, , ^2J = 1.7 Hz, 2H, *H*-e), 3.26 – 3.24 (m, 4H, *H*-c), 3.00 - 2.67 (m, 4H, *H*-k) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 153.7 (*C*-i), 138.7 (*C*-b), 137.0 (*C*-d), 129.7 (*C*-a), 128.1 (*C*-j), 126.9 (*C*-g), 119.2 (*C*-h), 116.1 (*C*-e,f), 39.5 (*C*-c), 31.8 (*C*-k) ppm.
IR (ATR): $\tilde{\nu}$ = 3076 (w), 2896 (w, br), 1637 (m), 1604 (m), 1482 (m), 1431 (w), 1288 (w), 1226 (w), 1147 (w), 1090 (w), 993 (s), 911 (s), 823 (s), 802 (s), 747 (m) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{20}H_{20}N_2]^+$ 288.16210; found 288.16242, 178.1 (100).
R_f: 0.38 (DCM), 0.17 (cyclohexane/DCM 3/2).

(*Z*)-3,8-Di-*p*-tolyl-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**35**)



Stille cross-coupling reaction:

Compound **35** was synthesized according to the general procedure from 4-bromotoluene (34.2 mg, 200 µmol). The product **35** was obtained after purification via column chromatography on silica (eluent: DCM) as a yellow solid (32.8 mg, 84.3 µmol, 84%).

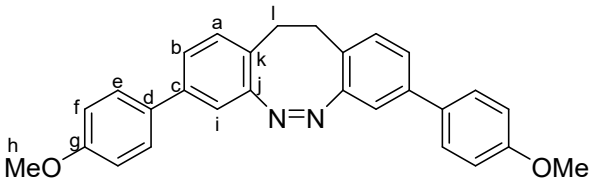
Suzuki cross-coupling reaction:

Compound **35** was synthesized according to the general procedure from 4-bromotoluene (34.2 mg, 200 µmol). The product **35** was obtained after purification via column chromatography on silica (eluent: DCM) as a yellow solid (29.9 mg, 77.1 µmol, 77%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.39 (d, ^3J = 8.2 Hz, 4H, *H*-e), 7.25 (dd, ^3J = 7.9 Hz, ^4J = 2.0 Hz, 2H, *H*-b), 7.19 (d, ^3J = 8.2 Hz, 4H, *H*-f), 7.08 (ad, ^4J = 2.0 Hz, 2H, *H*-i), 7.06 (d, ^3J = 7.9 Hz, 2H, *H*-a), 3.11 – 2.78 (m, 4H, *H*-l), 2.35 (s, 6H, *H*-h) ppm.

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 155.8 (*C*-j), 139.8 (*C*-c), 137.5 (*C*-g), 137.1 (*C*-d), 130.3 (*C*-a), 129.6 (*C*-f), 126.9 (*C*-e), 126.9 (*C*-k), 125.7 (*C*-b), 117.4 (*C*-i), 31.6 (*C*-l), 21.2 (*C*-h) ppm.
IR (ATR): $\tilde{\nu}$ = 2915 (w, br), 1520 (w), 1486 (m), 1457 (w), 1431 (w), 1383 (w), 1019 (w), 895 (m), 840 (w), 810 (s), 799 (s) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{28}H_{24}N_2]^+$ 388.19340; found 388.19354, 359.9 (100).
Mp: 187 °C**.**
R_f: 0.74 (DCM).

(*Z*)-3,8-Bis(4-methoxyphenyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**36**)



Stille cross-coupling reaction:

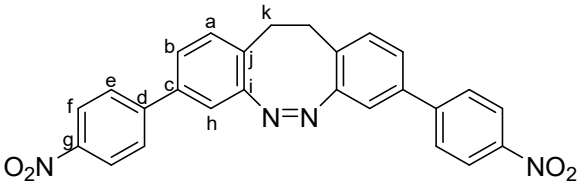
Compound **36** was synthesized according to the general procedure from 4-bromoanisole (37.4 mg, 200 µmol). The product **36** was obtained after purification via column chromatography on silica (eluent: DCM) as a yellow solid (29.9 mg, 71.0 µmol, 71%).

Suzuki cross-coupling reaction:

Compound **36** was synthesized according to the general procedure from 4-bromoanisole (37.4 mg, 200 µmol). The product **36** was obtained after purification via column chromatography on silica (eluent: DCM) as a yellow solid (32.8 mg, 78.1 µmol, 78%).

^1H NMR (600 MHz, $CDCl_3$) δ = 7.43 (d, ^3J = 8.8 Hz, 4H, *H*-e), 7.22 (dd, ^3J = 8.0 Hz, ^4J = 1.9 Hz, 2H, *H*-b), 7.06 – 7.04 (m, 4H, *H*-a/i), 6.91 (d, ^3J = 8.8 Hz, 4H, *H*-f), 3.81 (s, 6H, *H*-h), 3.07 – 2.78 (m, 4H, *H*-l) ppm.
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 159.5 (*C*-g), 155.8 (*C*-j), 139.5 (*C*-c), 132.5 (*C*-d), 130.3 (*C*-a), 128.1 (*C*-e), 126.5 (*C*-k), 125.4 (*C*-b), 117.1 (*C*-i), 114.3 (*C*-f), 55.5 (*C*-h), 31.6 (*C*-l) ppm.
IR (ATR): $\tilde{\nu}$ = 3004 (w, br), 2836 (w, br), 1606 (m), 1578 (w), 1520 (m), 1486 (s), 1437 (m), 1294 (m), 1247 (s), 1182 (s), 1116 (w), 1042 (m), 1021 (s), 888 (m), 832 (s), 826 (s), 813 (s), 789 (m) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{28}H_{24}N_2O_2]^+$ 420.18323; found 420.18355, 391.9 (100).
Mp: 225 °C**.**
R_f: 0.38 (DCM).

(*Z*)-3,8-Bis(4-nitrophenyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**37**)



Stille cross-coupling reaction:

Compound **37** was synthesized according to the general procedure from 1-bromo-4-nitrobenzene (40.4 mg, 200 µmol). The product **37** was obtained after purification via column chromatography on silica (eluent: DCM) as a yellow solid (34.3 mg, 76.2 µmol, 76%).

Suzuki cross-coupling reaction:

Compound **37** was synthesized according to the general procedure from 1-bromo-4-nitrobenzene (40.4 mg, 200 µmol). The product **37** was obtained after purification via column chromatography on silica (eluent: DCM) as a yellow solid (37.5 mg, 83.3 µmol, 83%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.24 (d, ^{3}J = 8.9 Hz, 4H, *H*-f), 7.65 (d, ^{3}J = 8.9 Hz, 4H, *H*-e), 7.34 (dd, ^{3}J = 7.9 Hz, ^{4}J = 2.0 Hz, 2H, *H*-b), 7.17 (d, ^{3}J = 7.9 Hz, 2H, *H*-a), 7.16 (ad, ^{4}J = 2.0 Hz, 2H, *H*-h), 3.13 – 2.87 (m, 4H, *H*-k) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 155.9 (*C*-i), 147.4 (*C*-g), 146.1 (*C*-d), 137.6 (*C*-c), 130.9 (*C*-a), 129.0 (*C*-j), 127.7 (*C*-e), 126.3 (*C*-b), 124.3 (*C*-f), 118.0 (*C*-h), 31.6 (*C*-k) ppm.
IR (ATR): $\tilde{\nu}$ = 2925 (w, br), 1597 (m), 1510 (s), 1479 (m), 1339 (s), 1110 (m), 1014 (w), 981 (w), 933 (w), 895 (m), 855 (s), 839 (s), 820 (s), 809 (s), 752 (s) cm^{-1}.
HRMS (EI, 70 eV) *m/z* (%): $[M]^+$ calcd for $[C_{26}H_{18}N_4O_4]^+$ 450.13226; found 450.13230, 421.8 (100).
Mp: 212 °C**.**
R_f: 0.47 (DCM).

References

1. R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, P. Granger, R. E. Hoffman and K. W. Zilm, *Pure and Applied Chemistry*, 2008, **80**, 59-84.
2. *The ACS Style Guide: Effective Communication of Scientific Information*, American Chemical Society, Washington, DC, 3rd edn., 2006.
3. S. Schultzke, M. Walther and A. Staubitz, *Molecules*, 2021, **26**, 3916.
4. T. Tellkamp, J. Shen, Y. Okamoto and R. Herges, *Eur. J. Org. Chem.*, 2014, DOI: 10.1002/ejoc.201402541, 5456-5461.
5. D. Hugenbusch, M. Lehr, J. S. von Glasenapp, A. J. McConnell and R. Herges, *Angew. Chem. Int. Ed.*, 2023, **62**, e202212571.
6. D. R. Coulson, L. C. Satek and S. O. Grim, in *Inorganic Syntheses*, ed. F. A. Cotton, McGraw-Hill, Inc., 1972, DOI: 10.1002/9780470132449.ch23, pp. 121-124.
7. C. Cordovilla, C. Bartolomé, J. M. Martínez-Ilarduya and P. Espinet, *ACS Catal.*, 2015, **5**, 3040-3053.
8. V. Farina, V. Krishnamurthy and W. J. Scott, *Org. React.*, 1997, **50**, 1-652.
9. (a) L. Heintze, D. Schmidt, T. Rodat, L. Witt, J. Ewert, M. Kriegs, R. Herges and C. Peifer, *Int. J. Mol. Sci.*, 2020, **21**, 8961. (b) Q. Zhu, S. Wang and P. Chen, *Org. Lett.*, 2019, **21**, 4025-4029.
10. (a) E. R. Thapaliya, J. Zhao and G. C. R. Ellis-Davies, *ACS Chem. Neurosci.*, 2019, **10**, 2481-2488. (b) V. Farina, S. Kapadia, B. Krishnan, C. Wang and L. S. Liebeskind, *J. Org. Chem.*, 1994, **59**, 5905-5911.
11. J. Strueben, P. J. Gates and A. Staubitz, *J. Org. Chem.*, 2014, **79**, 1719-1728.
12. S. P. Mee, V. Lee and J. E. Baldwin, *Chem. Eur. J.*, 2005, **11**, 3294-3308.
13. J. R. Naber and S. L. Buchwald, *Adv. Synth. Catal.*, 2008, **350**, 957-961.

^{1}H, $^{13}C\{^{1}H\}$, ^{11}B, ^{19}F and ^{119}Sn NMR Spectra of the Purified Compounds

2,2'-(Ethane-1,2-diyl)bis(4-iodoaniline)

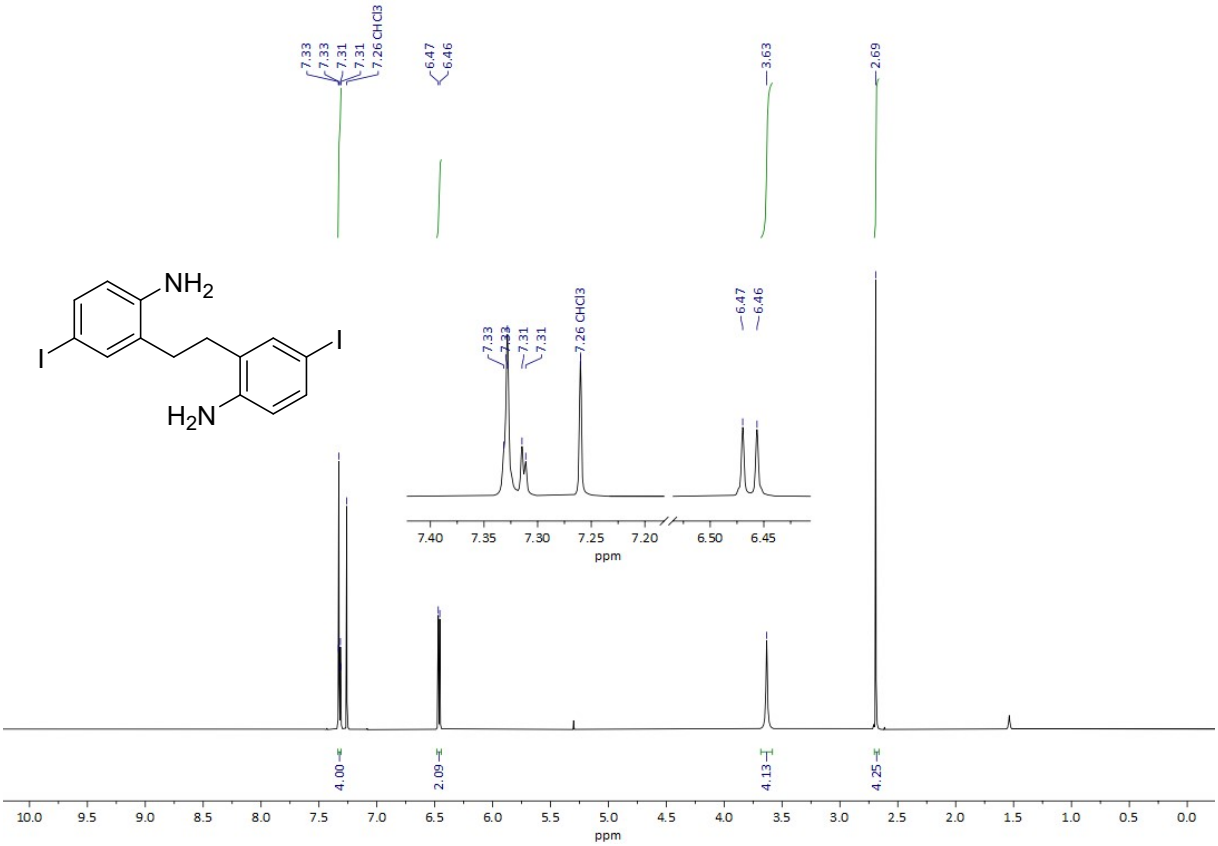


Figure 1: ^{1}H NMR spectrum of2,2'-(ethane-1,2-diyl)bis(4-iodoaniline) in $CDCl_3$.

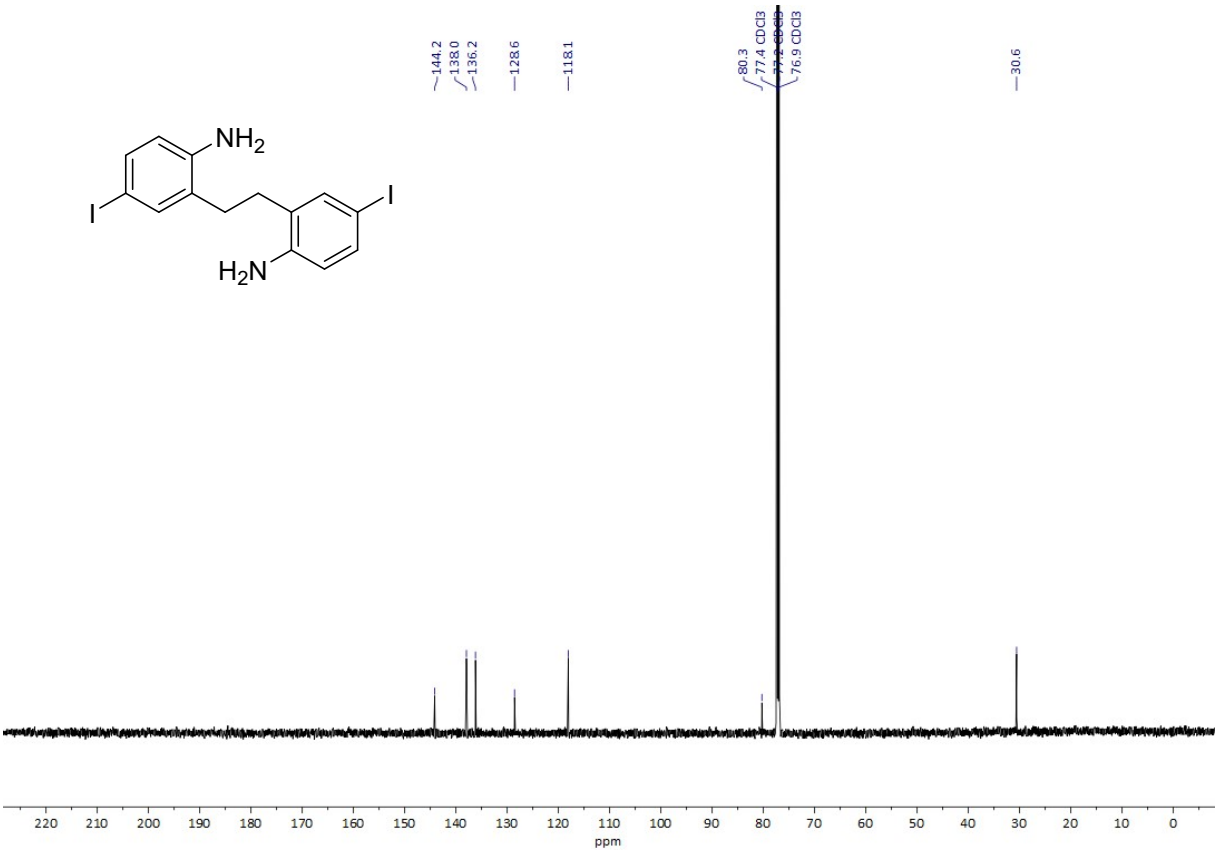


Figure 2: $^{13}C\{^{1}H\}$ NMR spectrum of 2,2'-(ethane-1,2-diyl)bis(4-iodoaniline) in $CDCl_3$.

(*Z*)-2,9-Diiodo-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**1**)

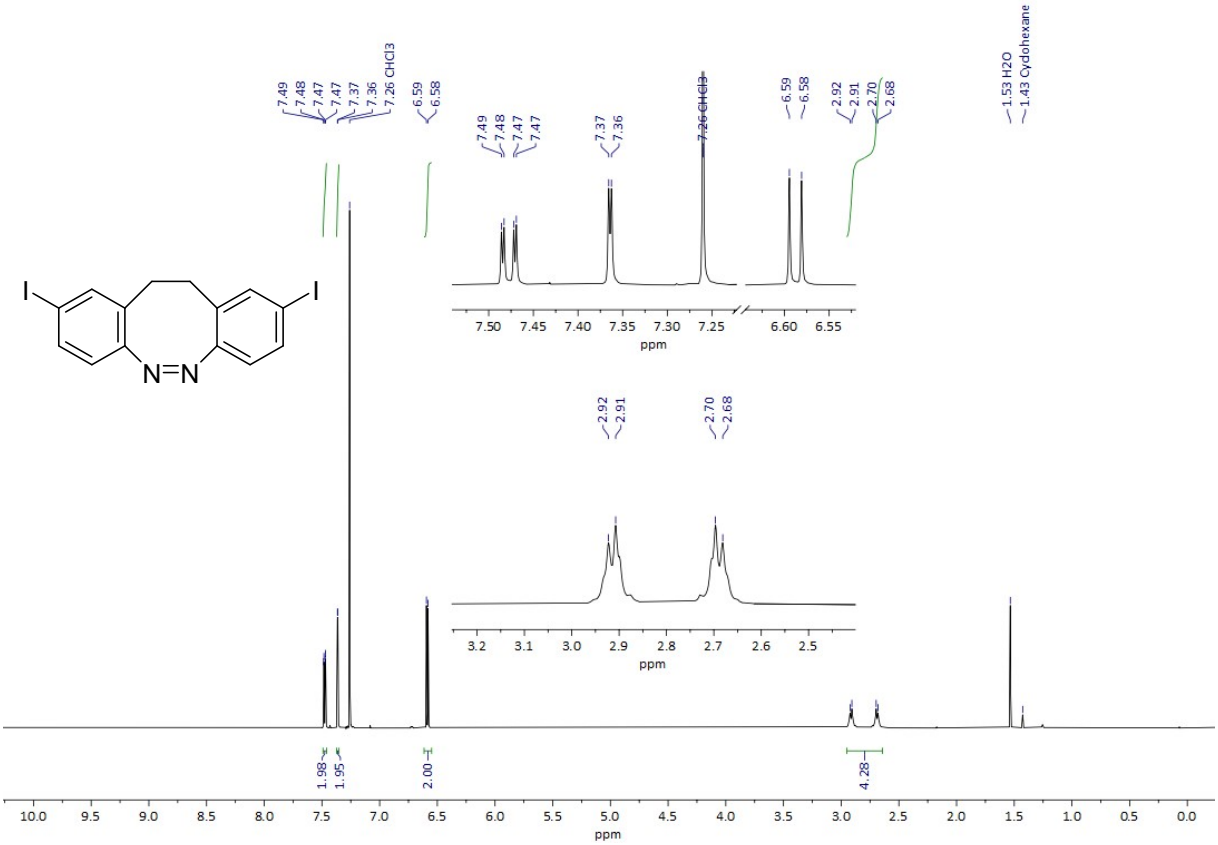


Figure 3: ^{1}H NMR spectrum of **1** in $CDCl_3$.

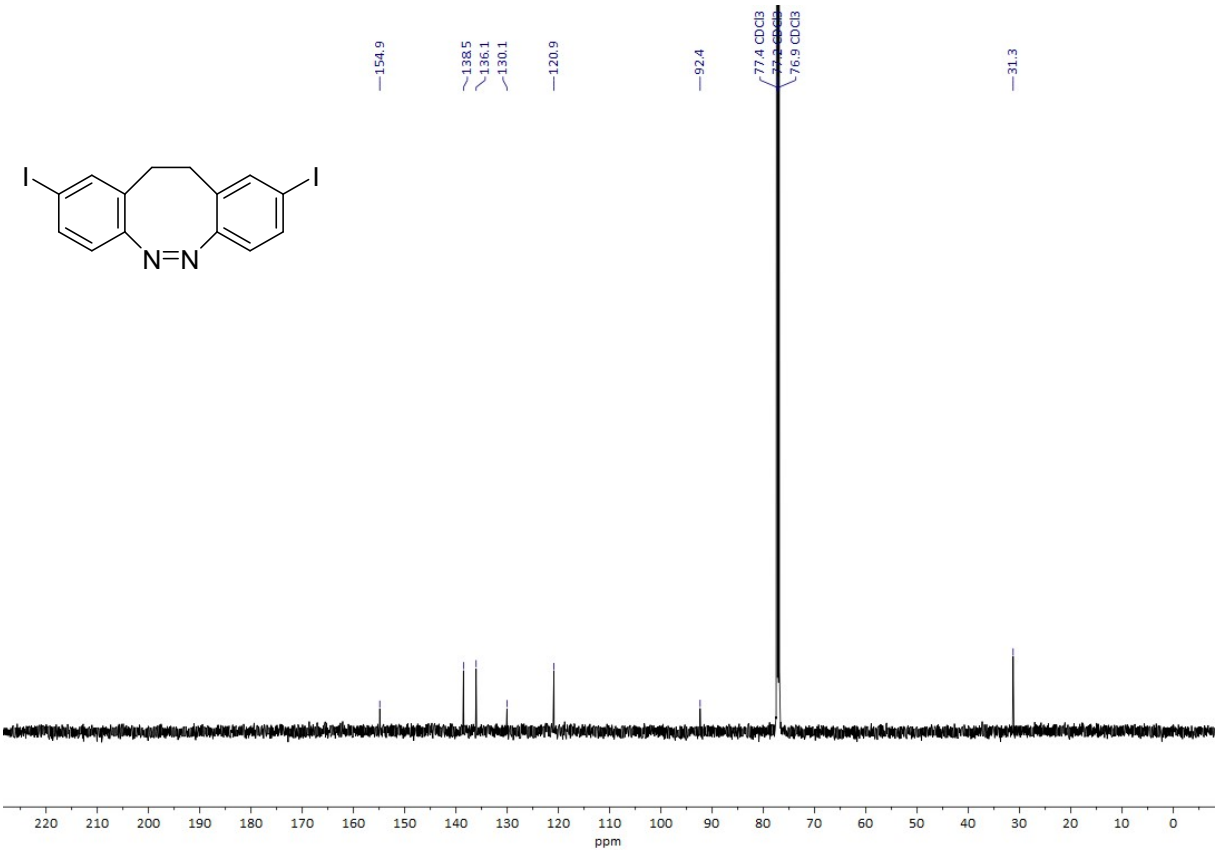


Figure 4: $^{13}C\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$.

5-Iodo-2-(4-iodo-2-nitrophenethyl)aniline

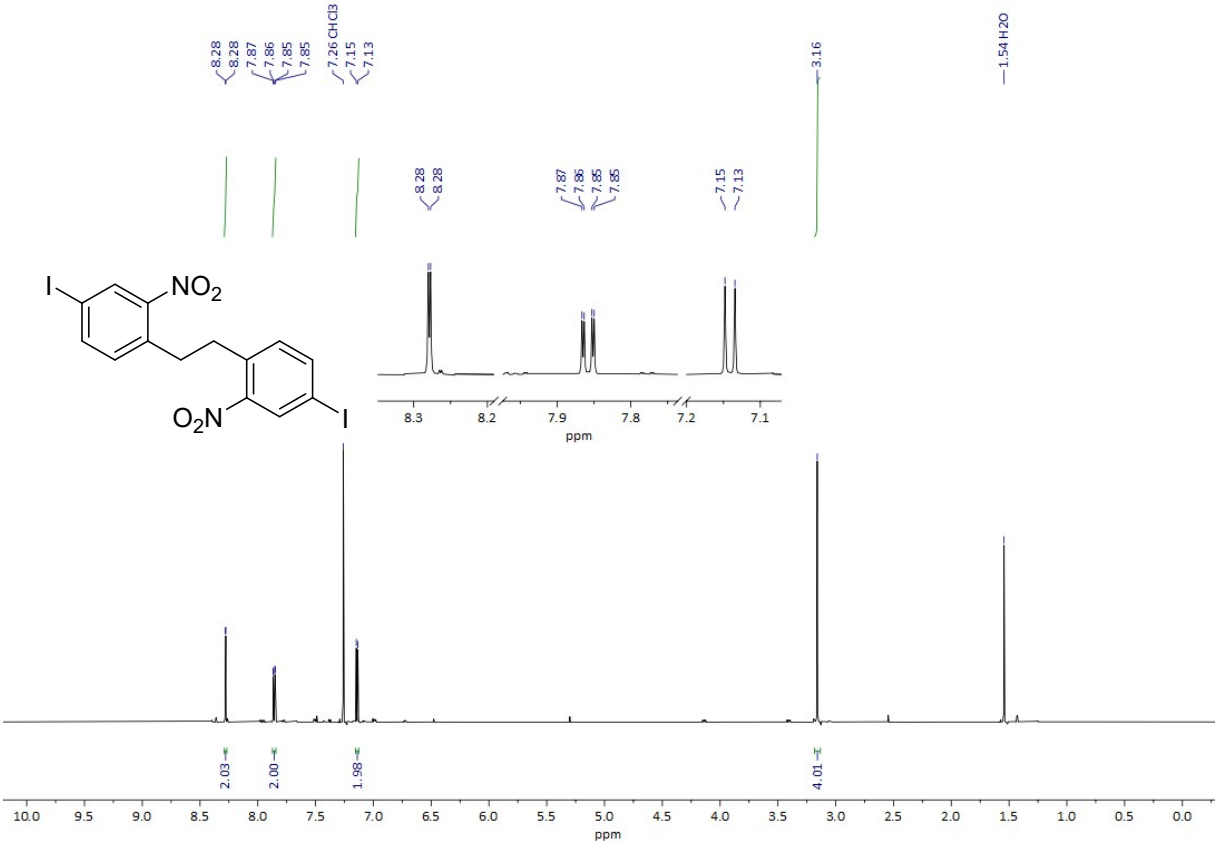


Figure 5: ^{1}H NMR spectrum of 5-iodo-2-(4-iodo-2-nitrophenethyl)aniline in $CDCl_3$.

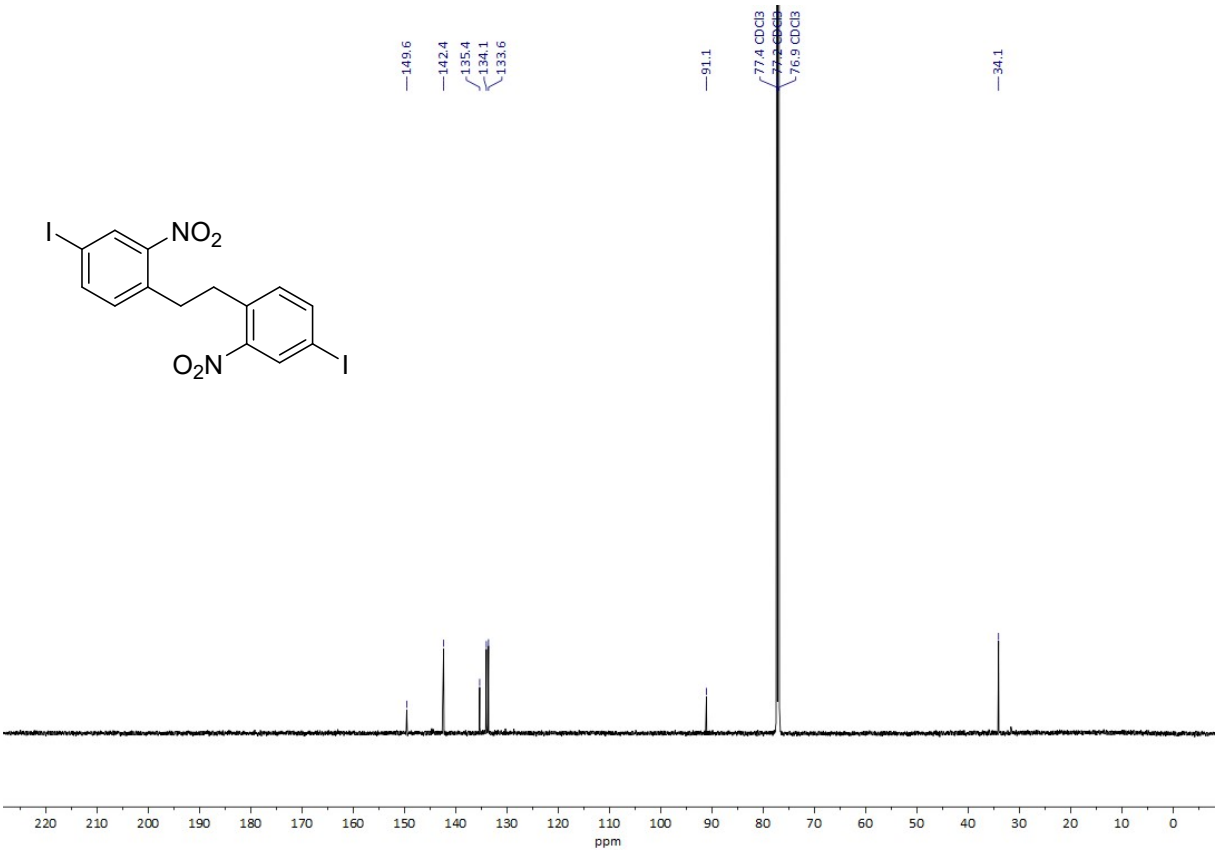


Figure 6: $^{13}C\{^{1}H\}$ NMR spectrum of 5-iodo-2-(4-iodo-2-nitrophenethyl)aniline in $CDCl_3$.

6,6'-(Ethane-1,2-diyl)bis(3-iodoaniline)

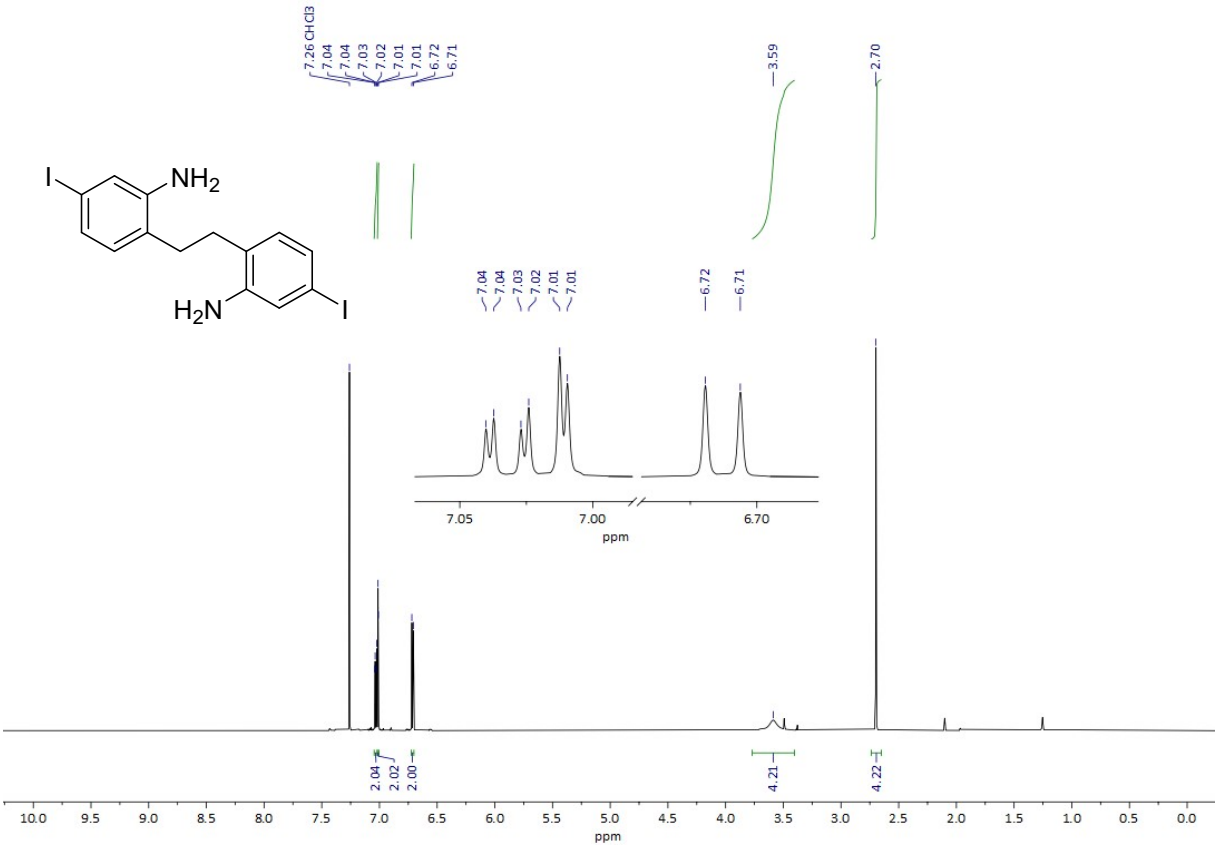


Figure 7: ^{1}H NMR spectrum of 6,6'-(ethane-1,2-diyl)bis(3-iodoaniline) in $CDCl_3$.

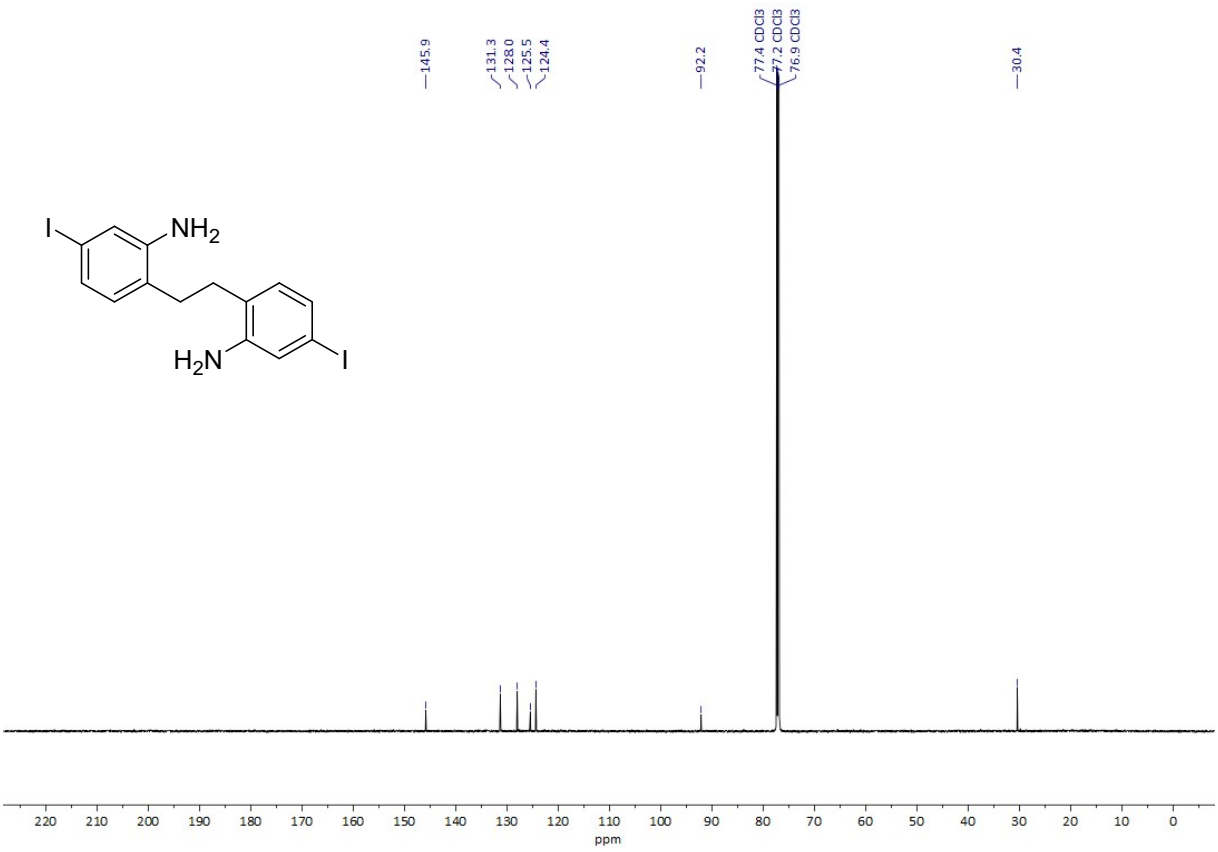


Figure 8: $^{13}C\{^{1}H\}$ NMR spectrum of 6,6'-(ethane-1,2-diyl)bis(3-iodoaniline) in $CDCl_3$.

(*Z*)-3,8-Diiodo-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**2**)

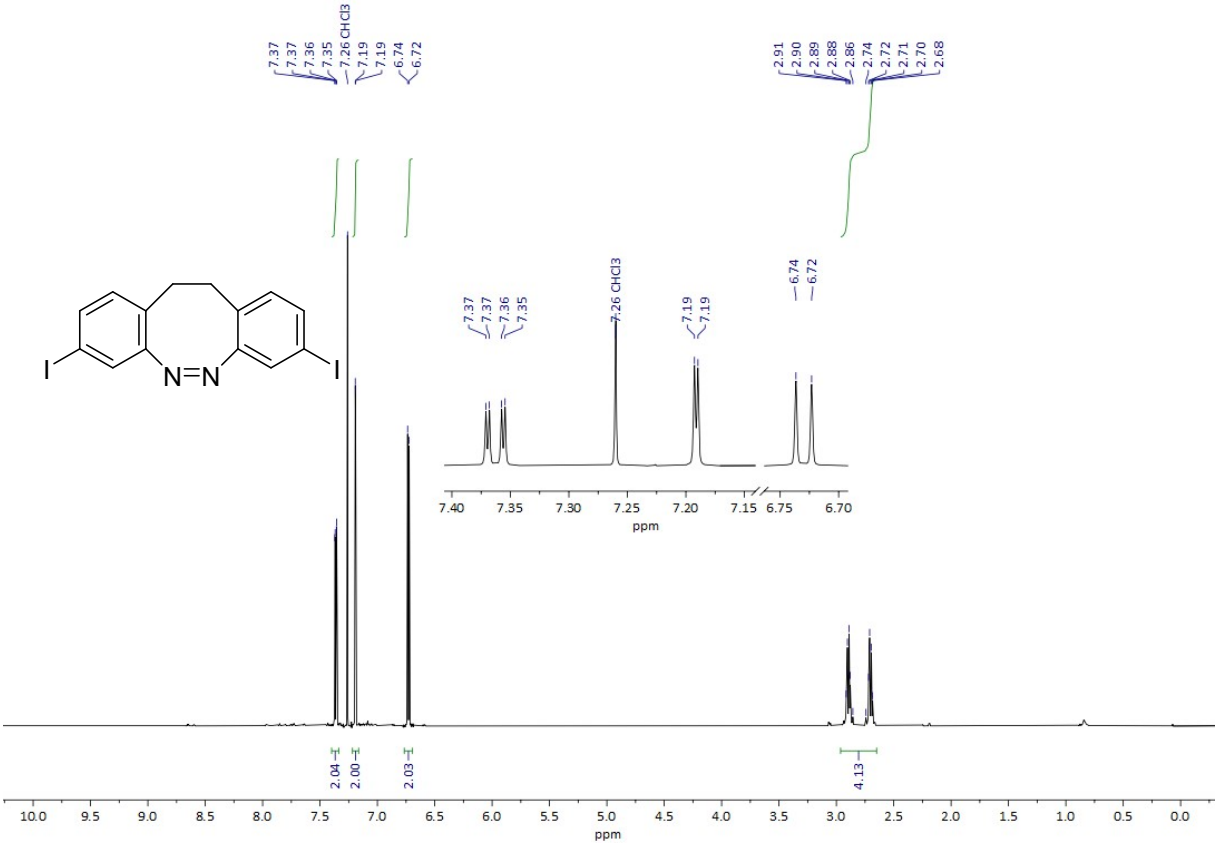


Figure 9: ^{1}H NMR spectrum of **2** in $CDCl_3$.

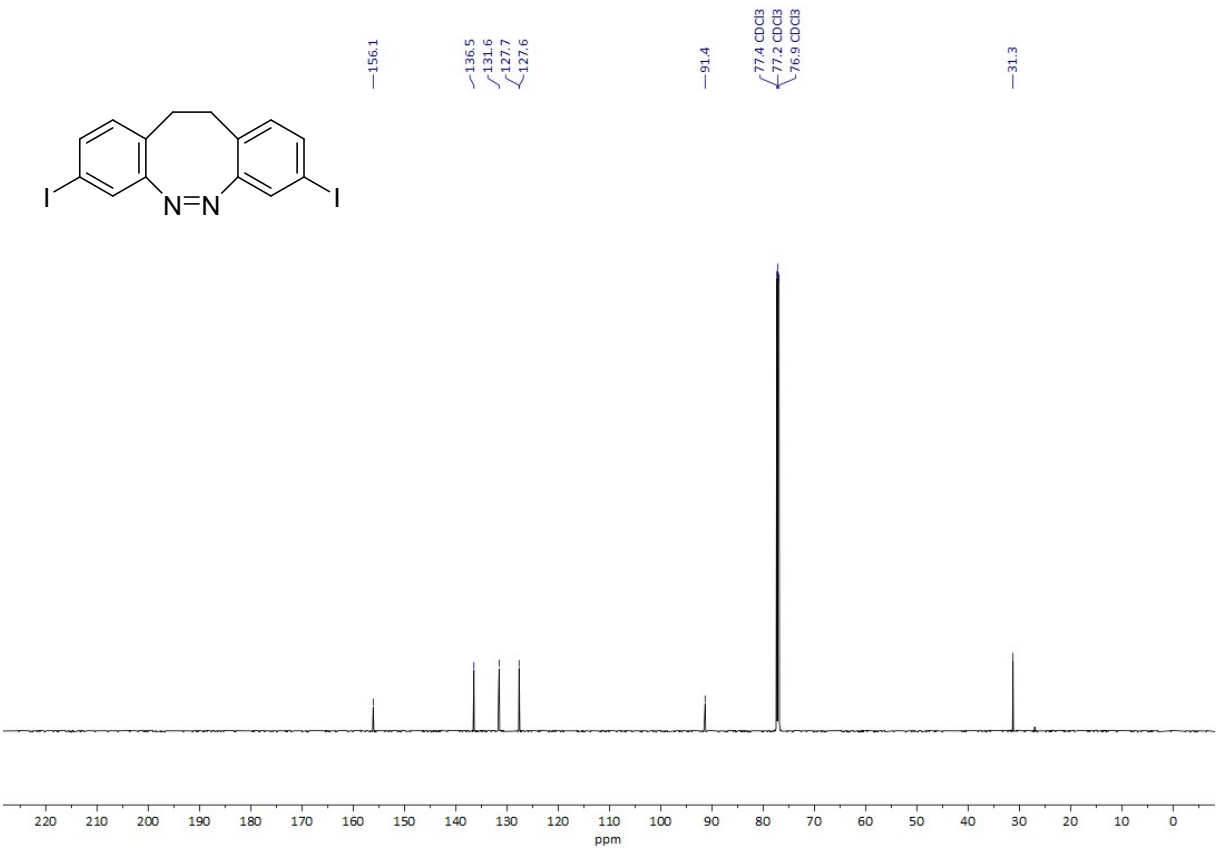


Figure 10: $^{13}C\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$.

(*Z*)-2,9-Bis(trimethylstannyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**3**)

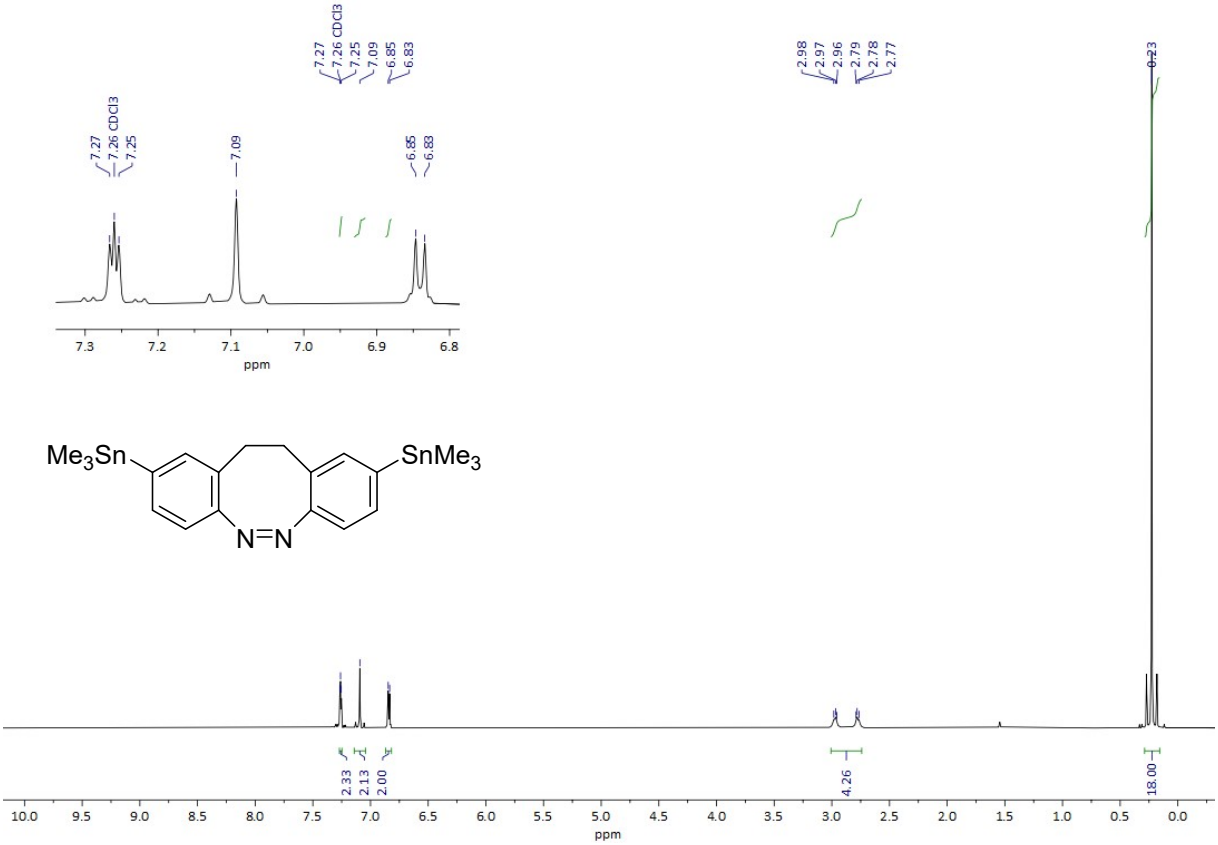


Figure 11: ^{1}H NMR spectrum of **3** in $CDCl_3$.

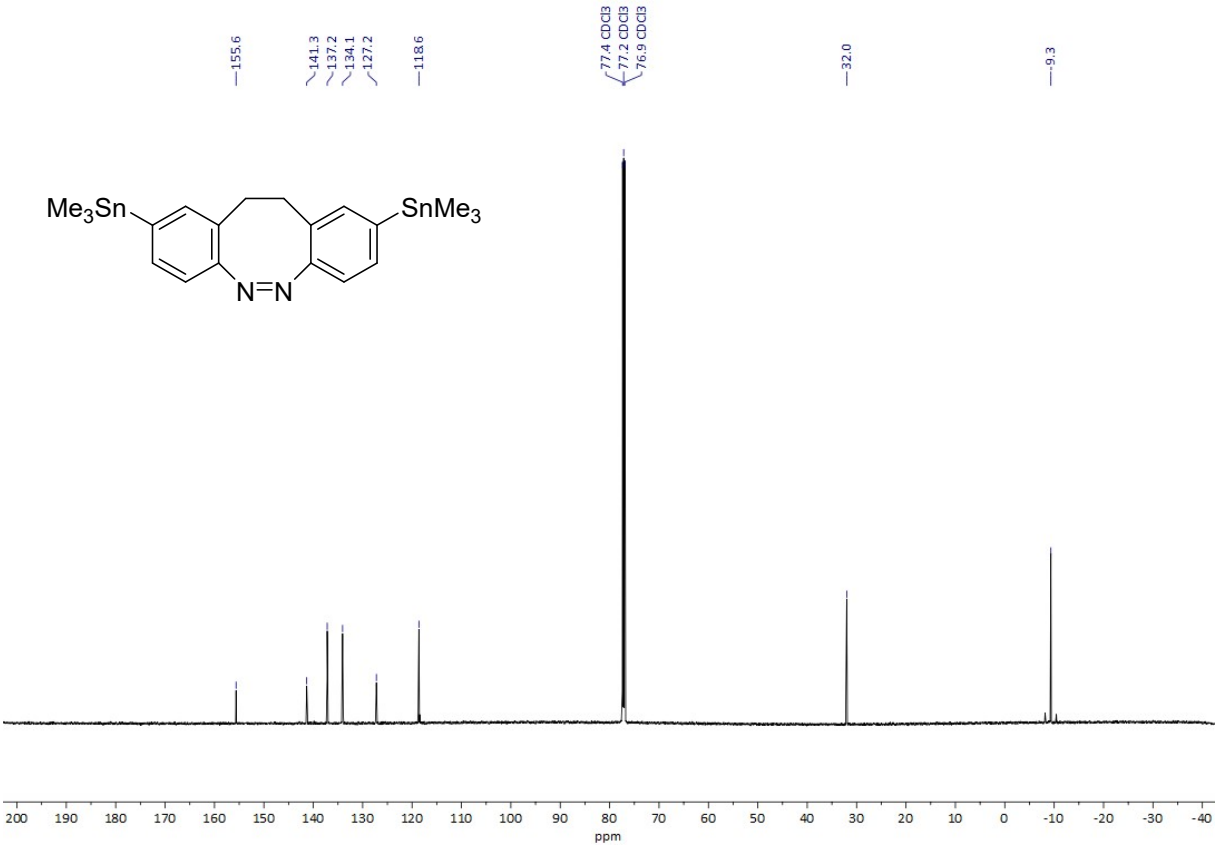


Figure 12: $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

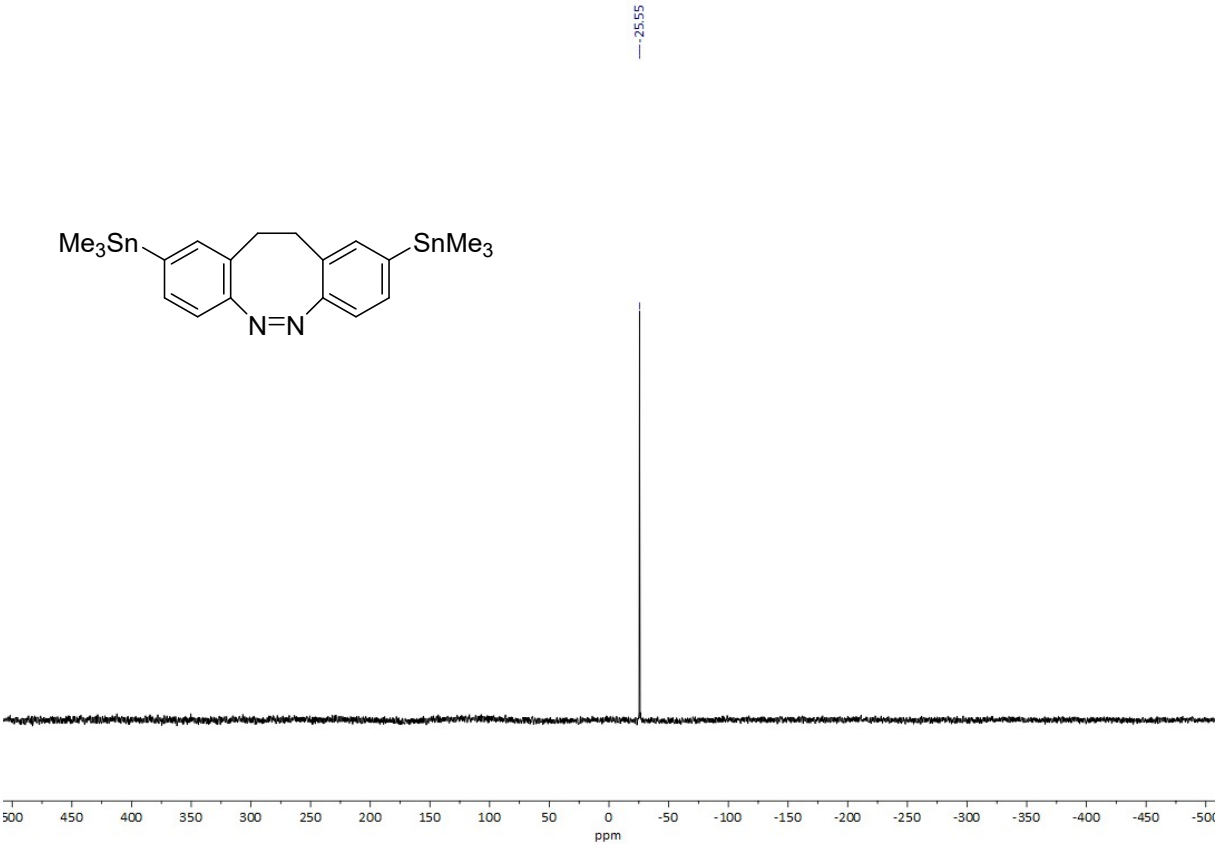


Figure 13: $^{119}Sn\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

(*Z*)-3,8-Bis(trimethylstannyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**4**)

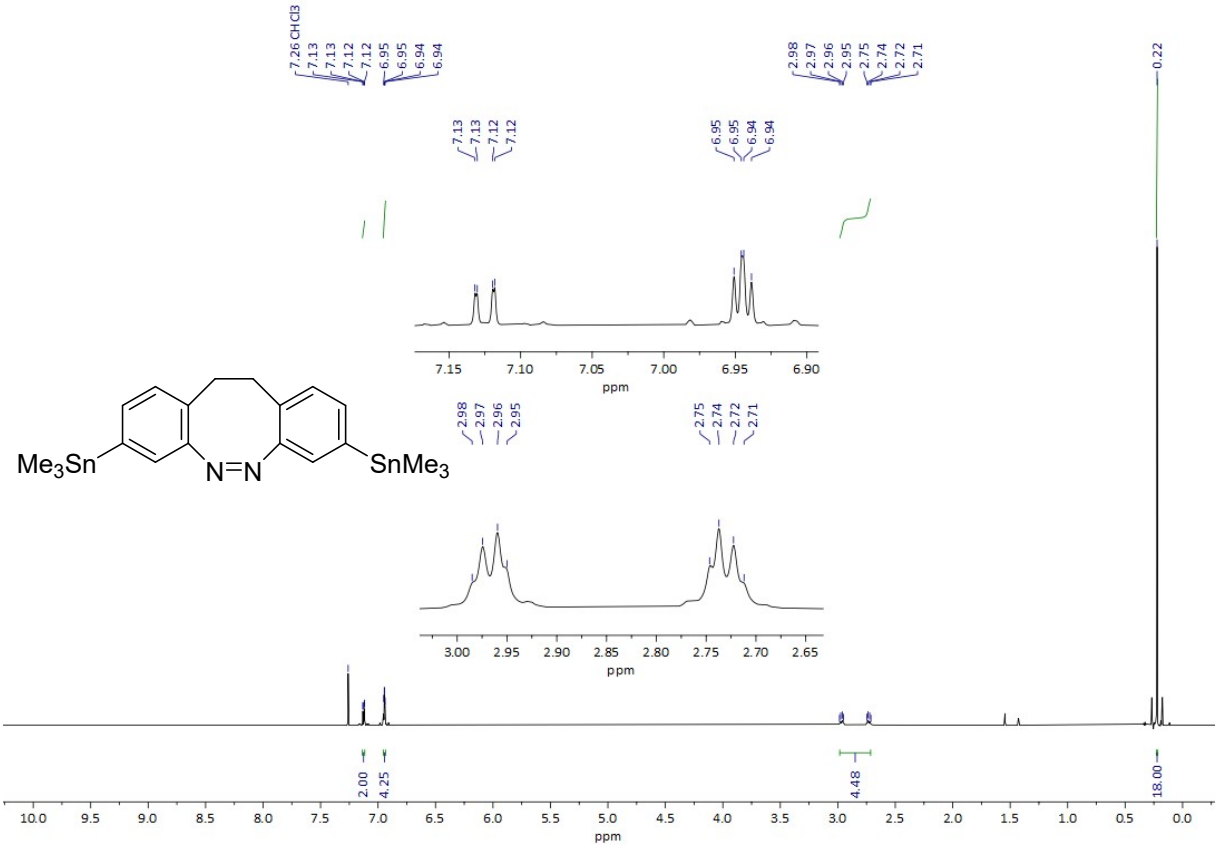


Figure 14: ^{1}H NMR spectrum of **4** in $CDCl_3$.

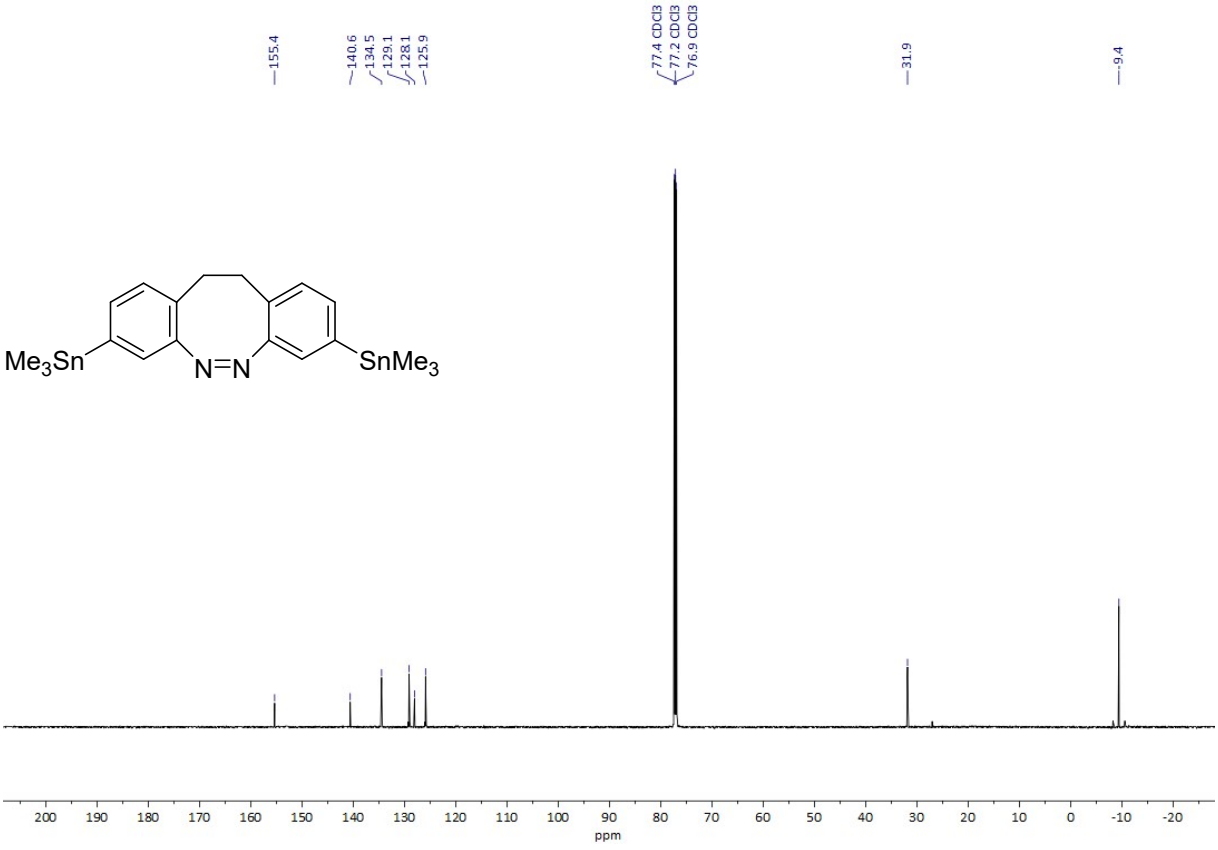


Figure 15: $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$.

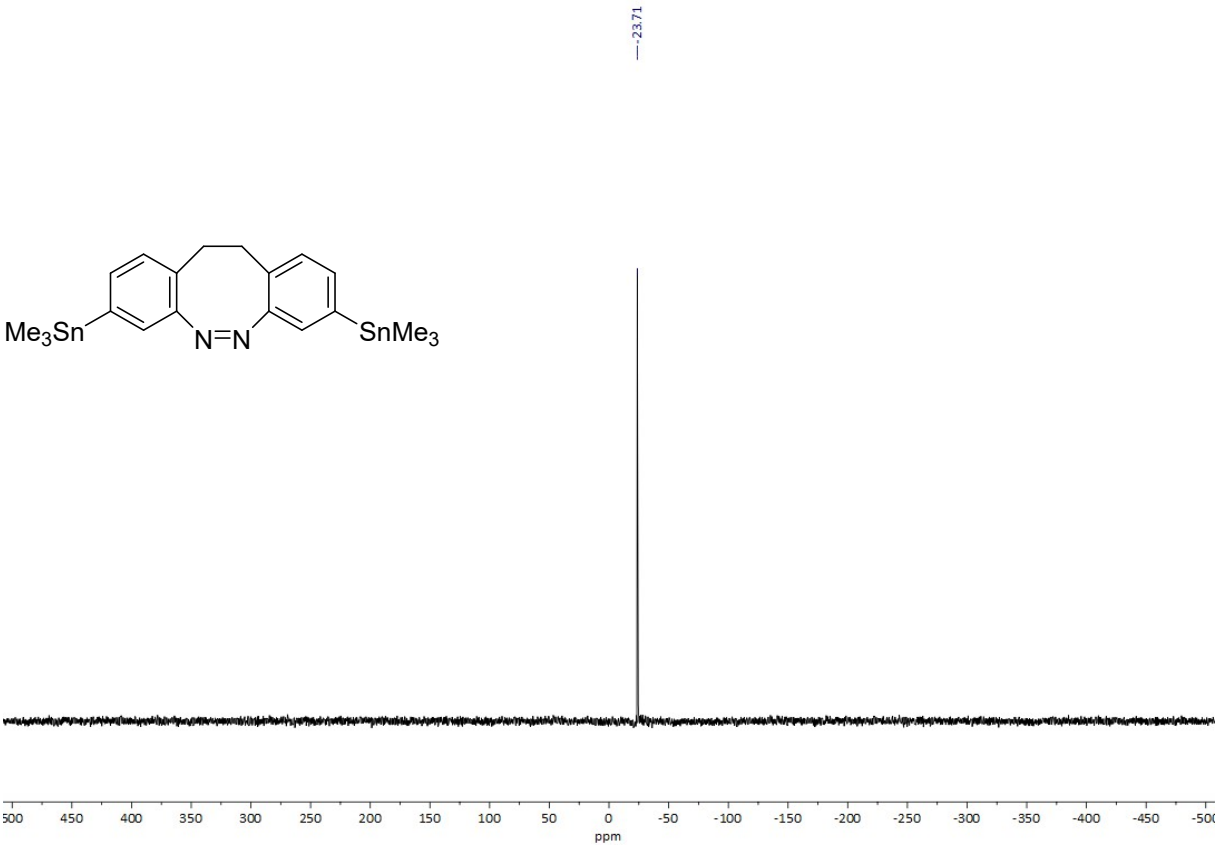


Figure 16: $^{119}Sn\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$.

(*Z*)-2,9-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**5**)

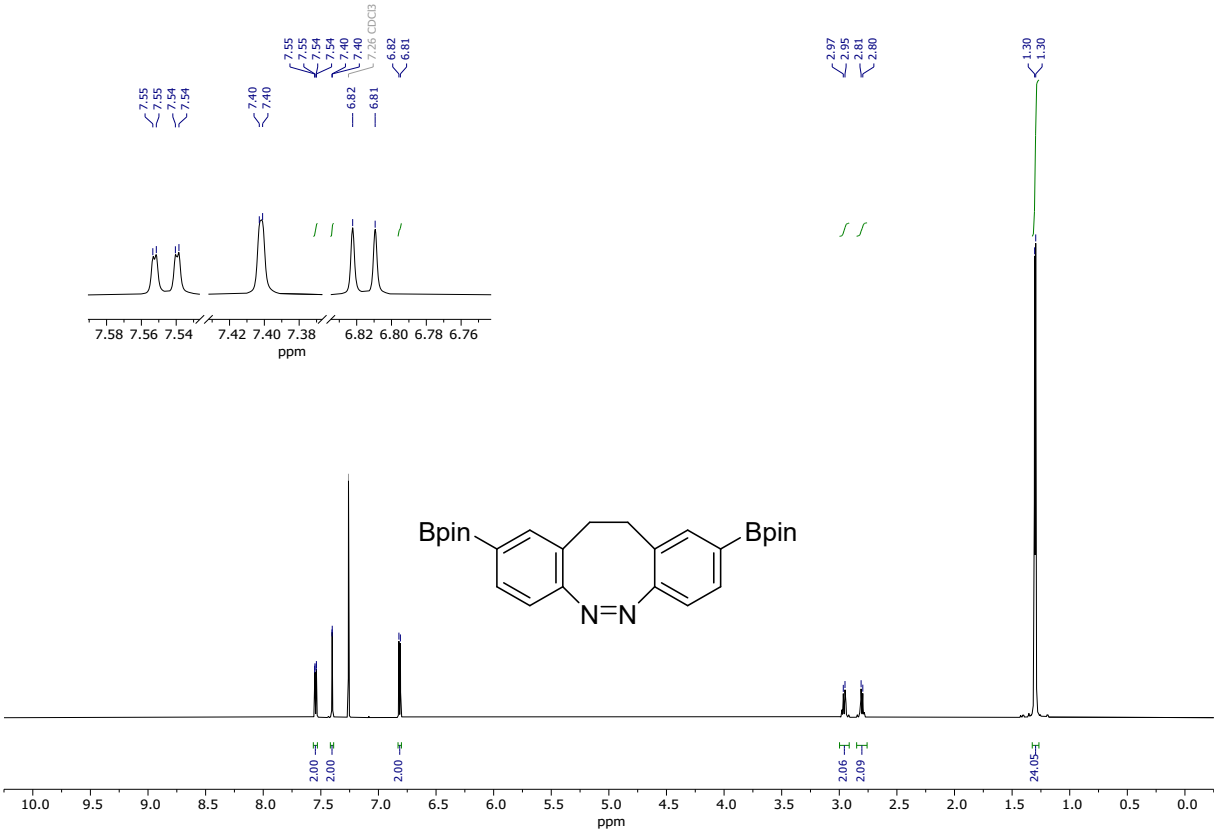


Figure 17: ^{1}H NMR spectrum of **5** in $CDCl_3$.

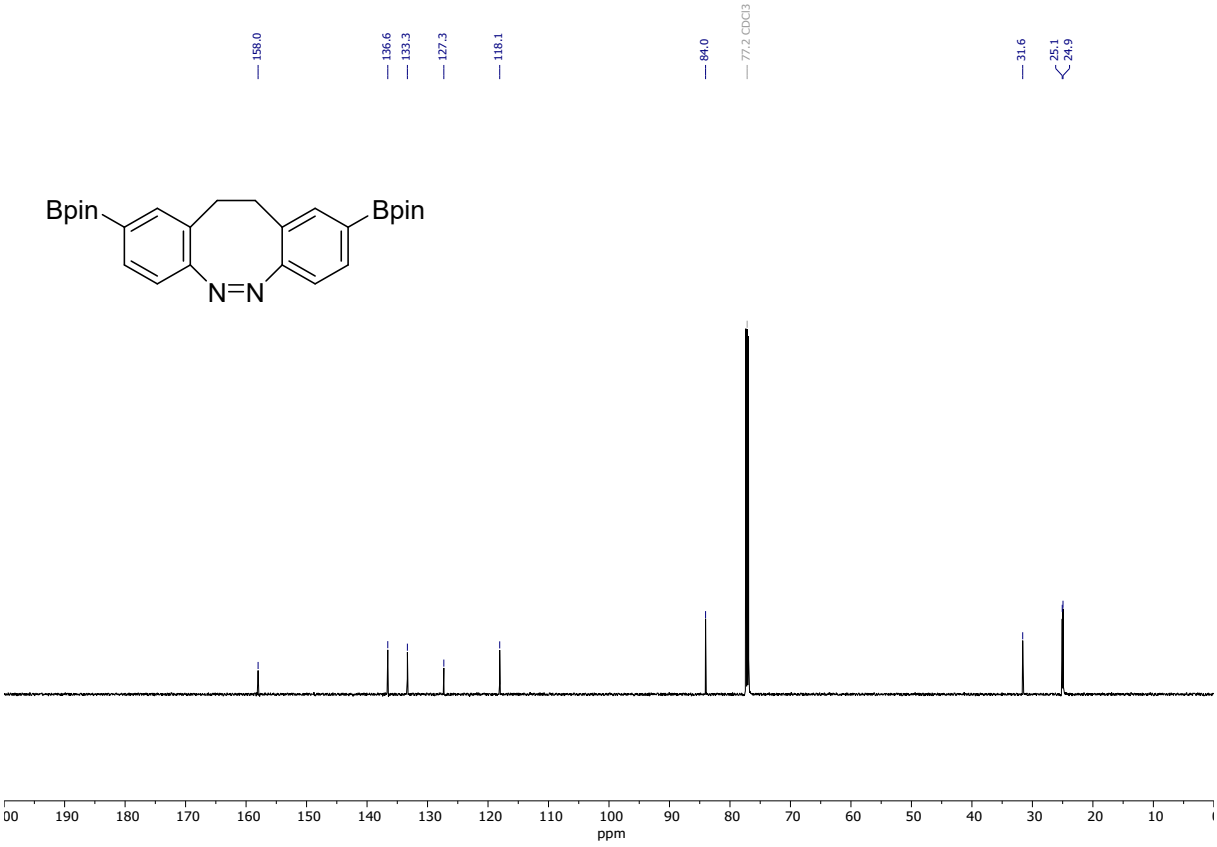


Figure 18: $^{13}C\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$.

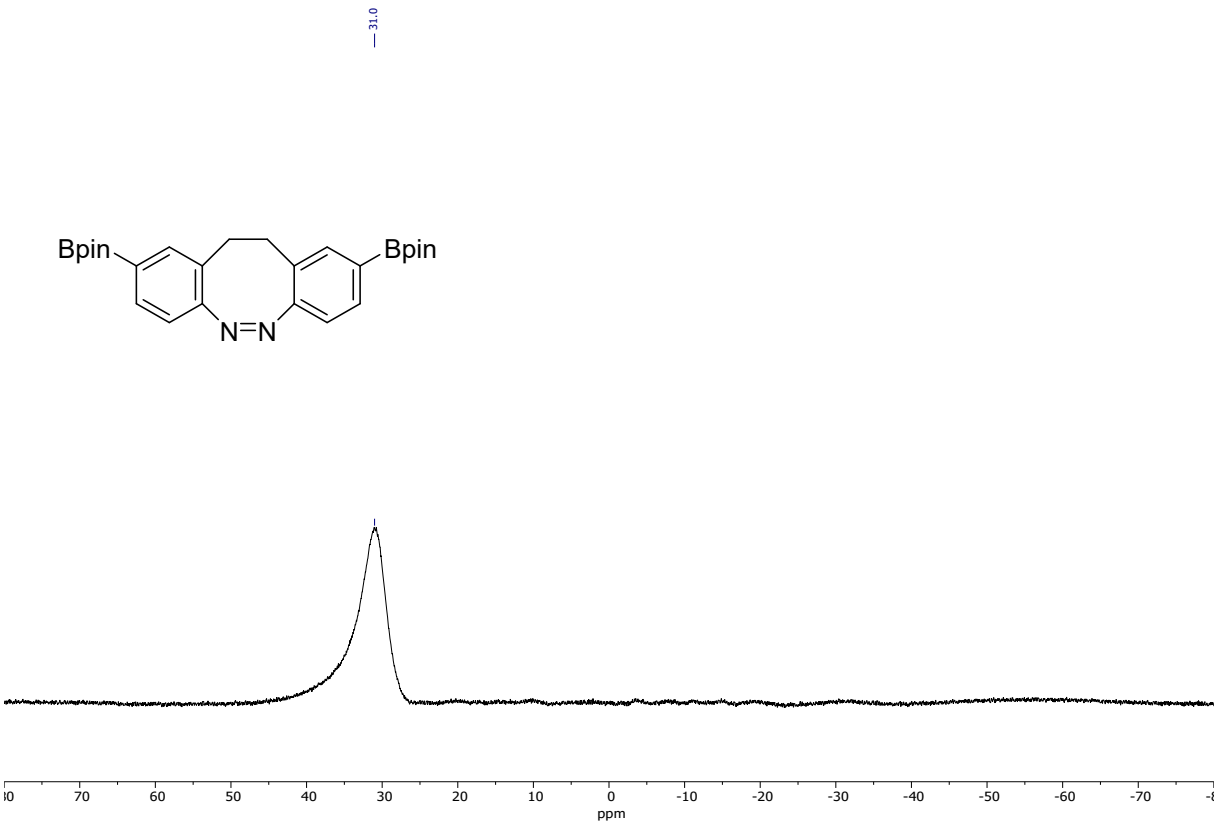


Figure 19: $^{11}B\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$.

2,9-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,6,11,12-tetrahydrodibenzo[c,g][1,2]diazocine

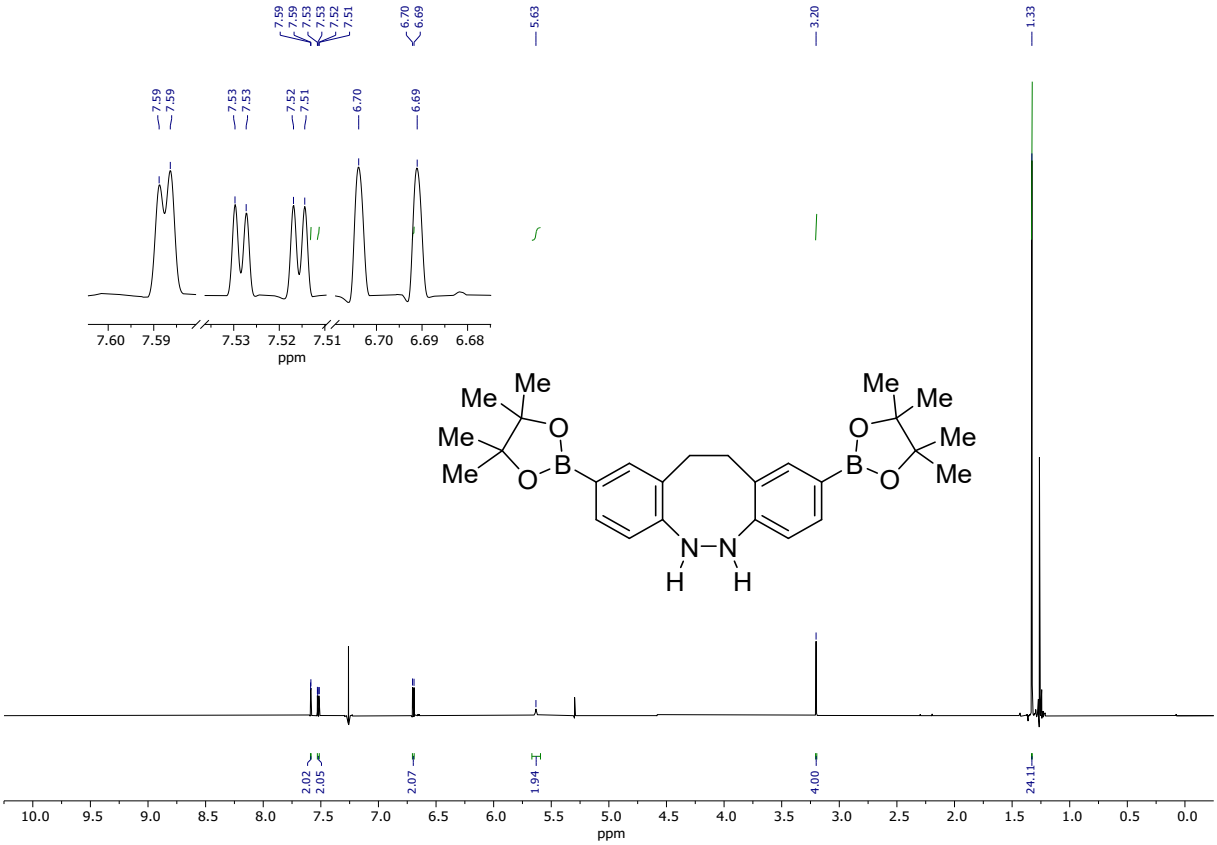


Figure 20: ^{1}H NMR spectrum of 2,9-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,6,11,12-tetrahydrodibenzo[c,g][1,2]diazocine in $CDCl_3$.

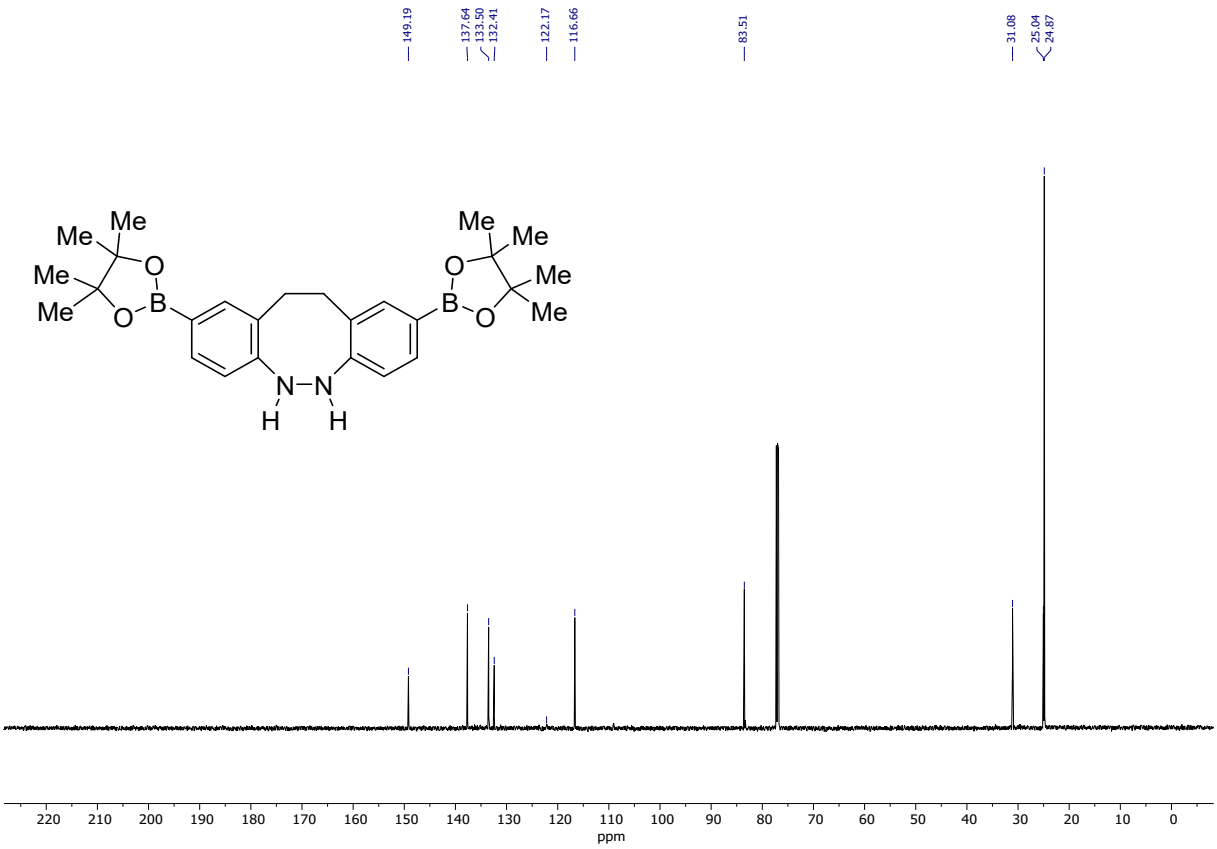


Figure 21: $^{13}C\{^{1}H\}$ NMR spectrum of 2,9-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,6,11,12-tetrahydrodibenzo[c,g][1,2]diazocine in $CDCl_3$.

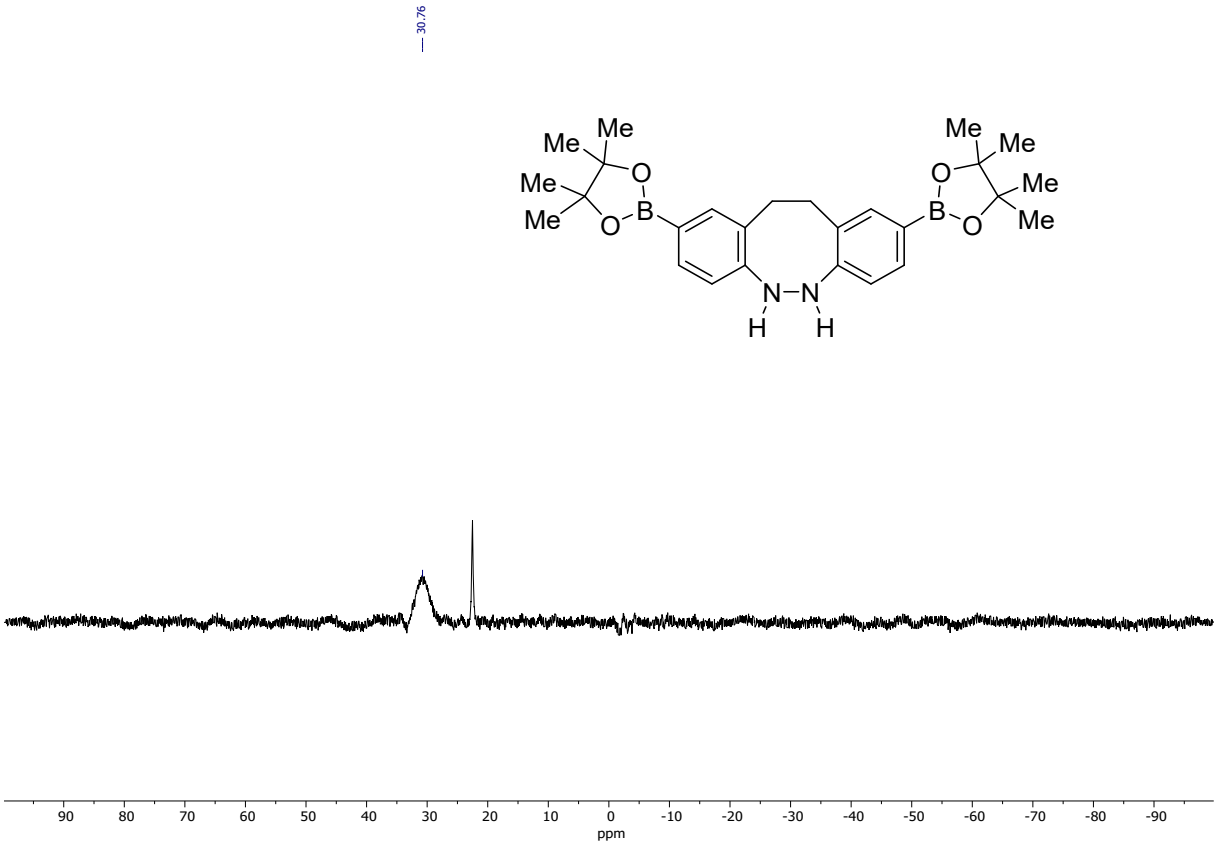


Figure 22: $^{11}B\{^{1}H\}$ NMR spectrum of 2,9-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,6,11,12-tetrahydrodibenzo[c,g][1,2]diazocine in $CDCl_3$.

(*Z*)-3,8-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**6**)

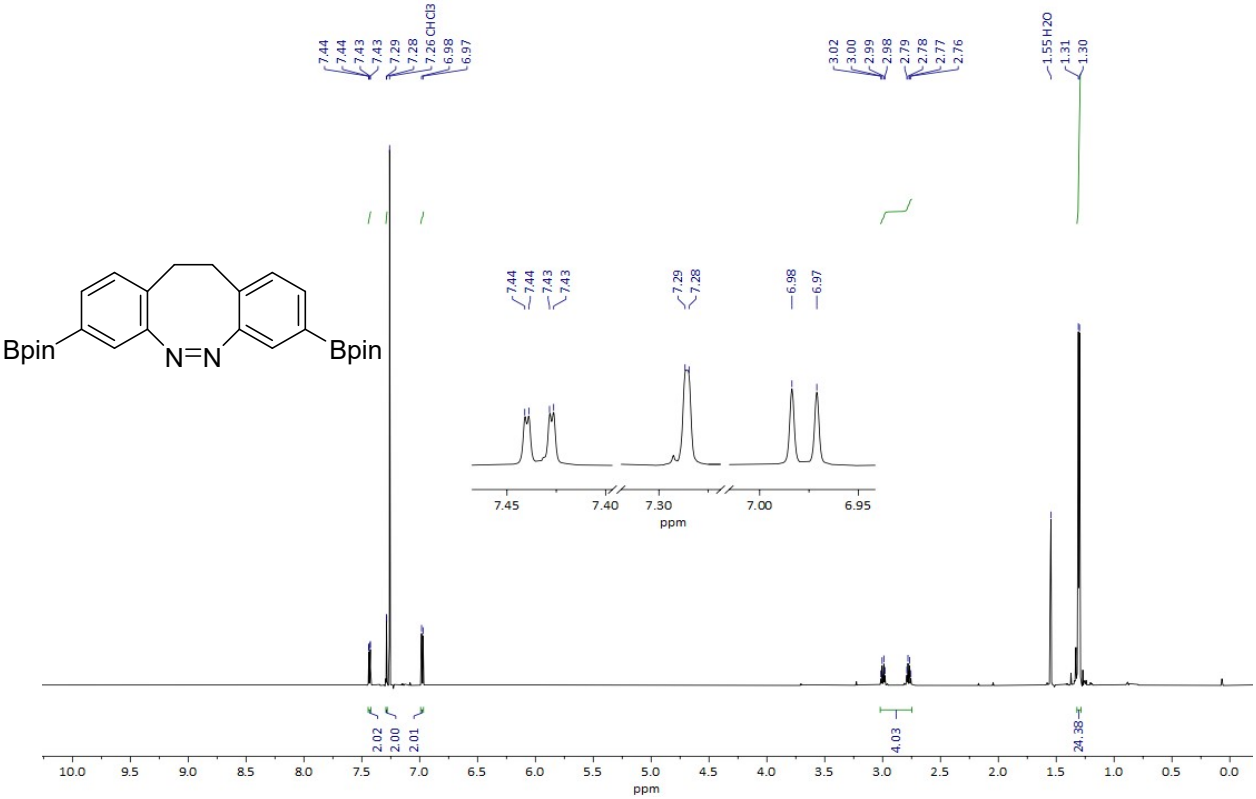


Figure 23: ^{1}H NMR spectrum of **6** in $CDCl_3$.

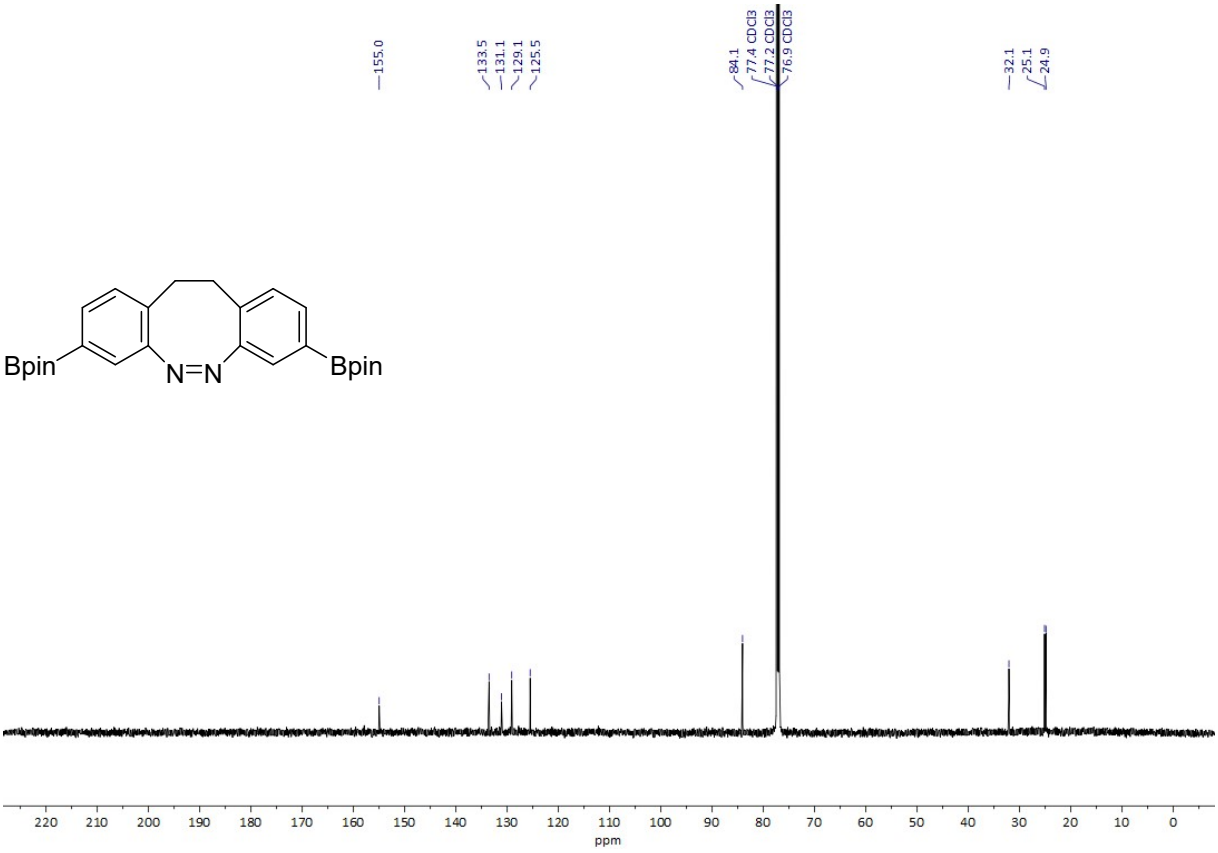


Figure 24: $^{13}C\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$.

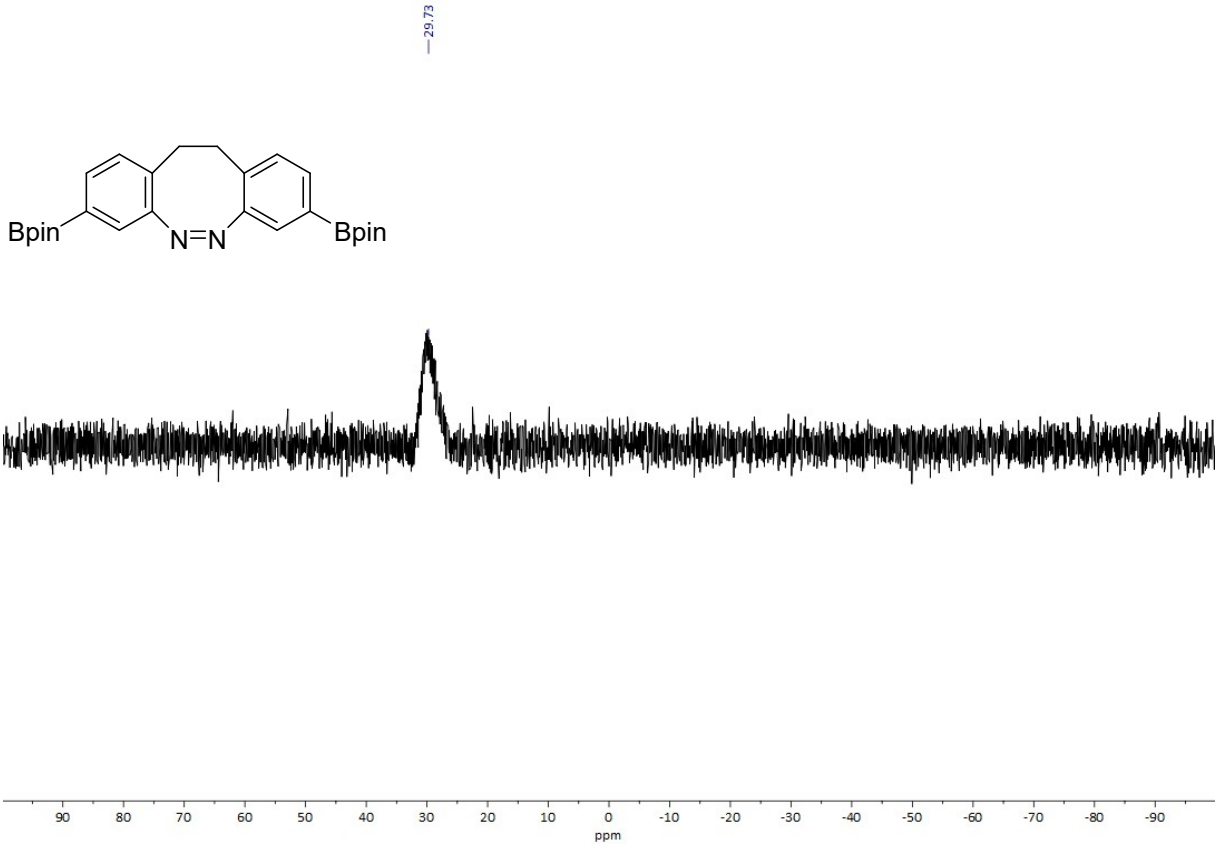


Figure 25: $^{11}B\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$.

(*Z*)-2,9-Di-*p*-tolyl-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**7**)

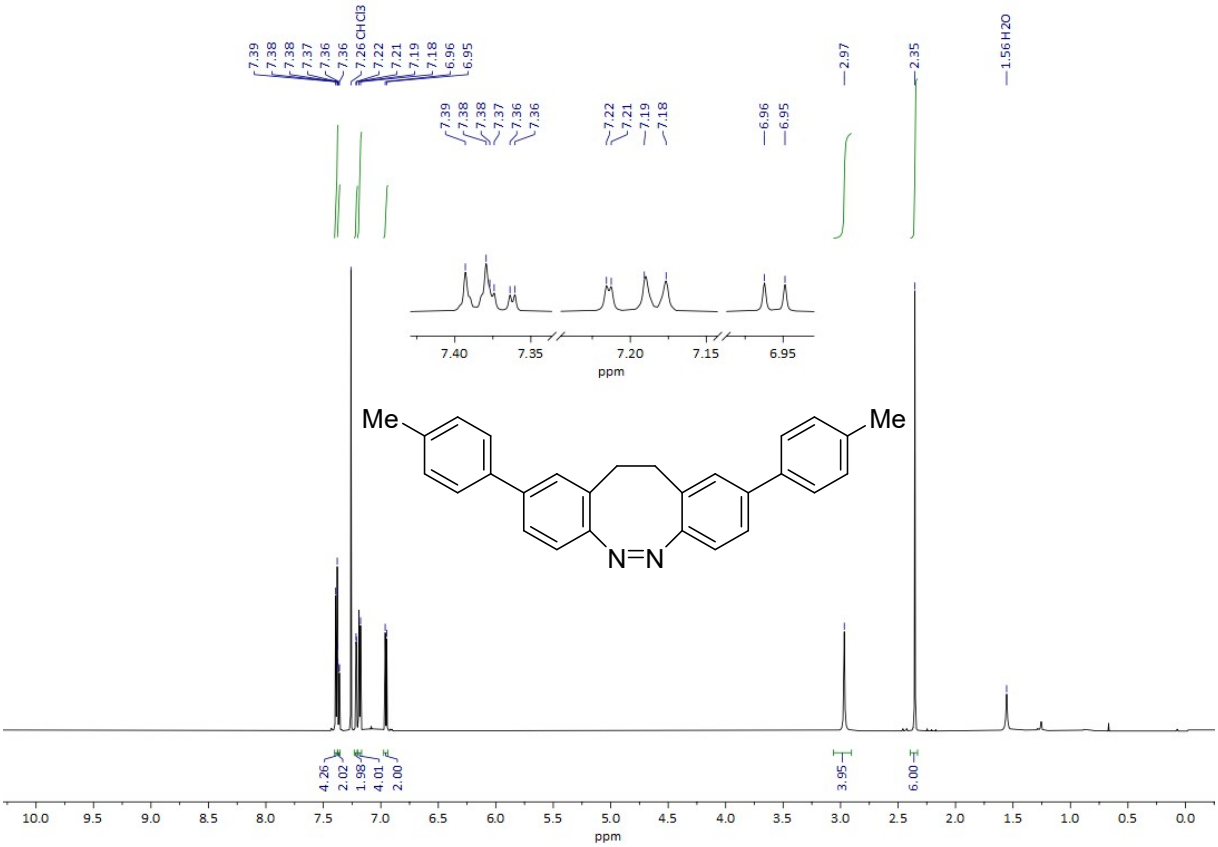


Figure 26: ^{1}H NMR spectrum of **7** in $CDCl_3$.

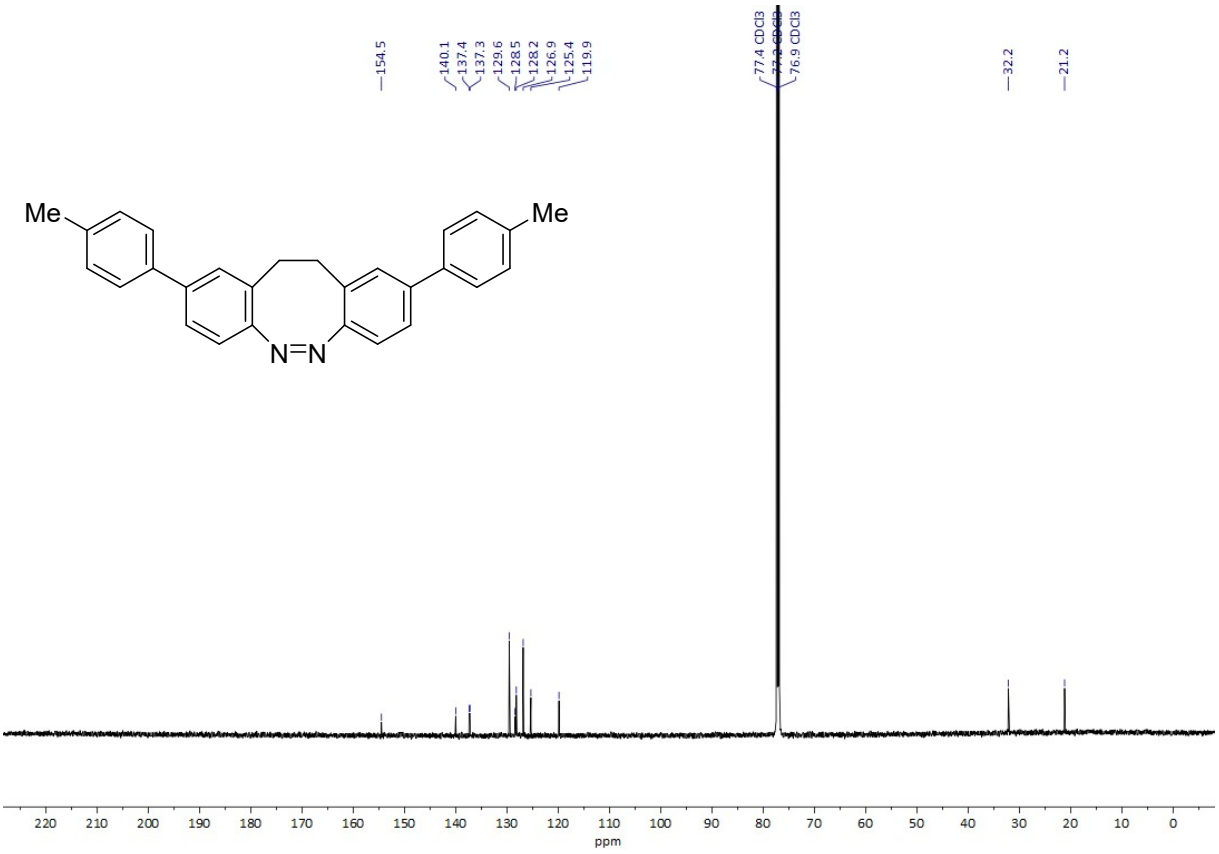


Figure 27: $^{13}C\{^{1}H\}$ NMR spectrum of **7** in $CDCl_3$.

(*Z*)-2,9-Bis(4-isopropylphenyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**8**)

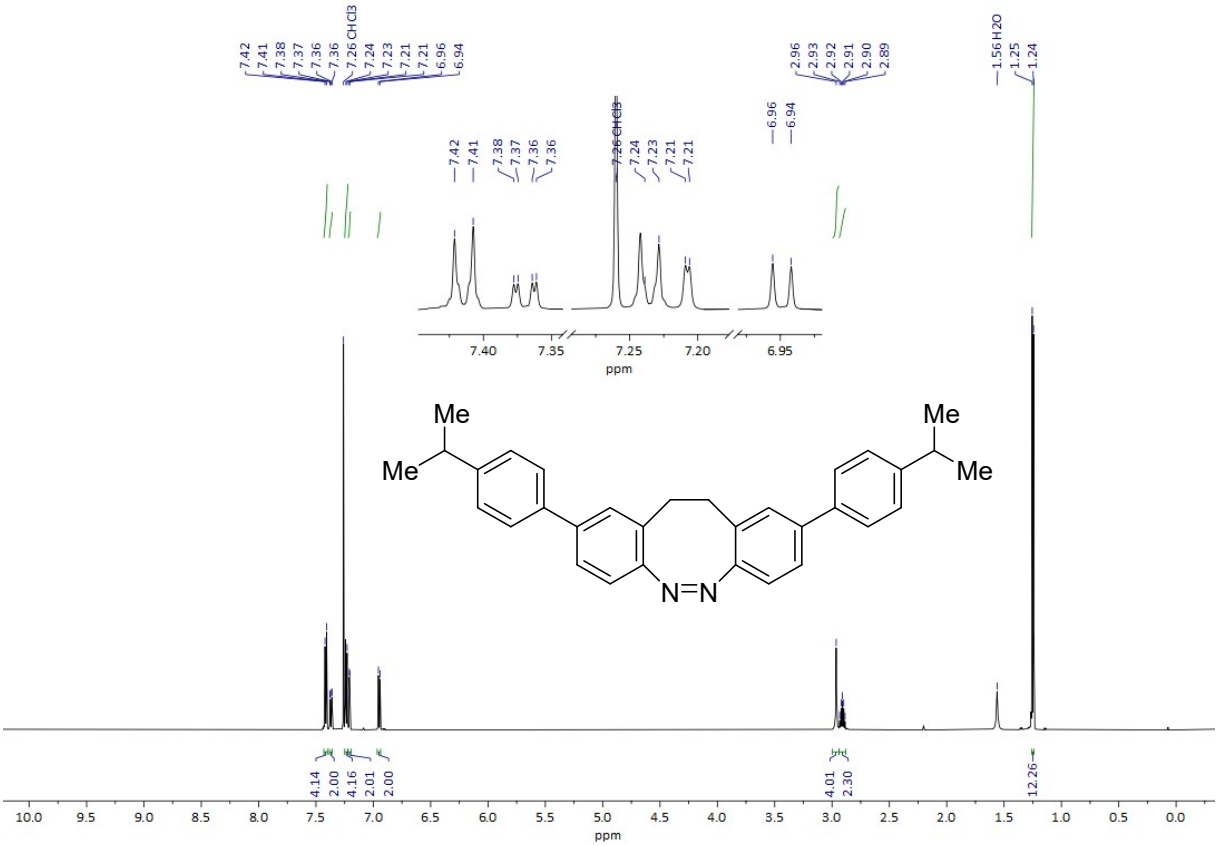


Figure 28: ^{1}H NMR spectrum of **8** in $CDCl_3$.

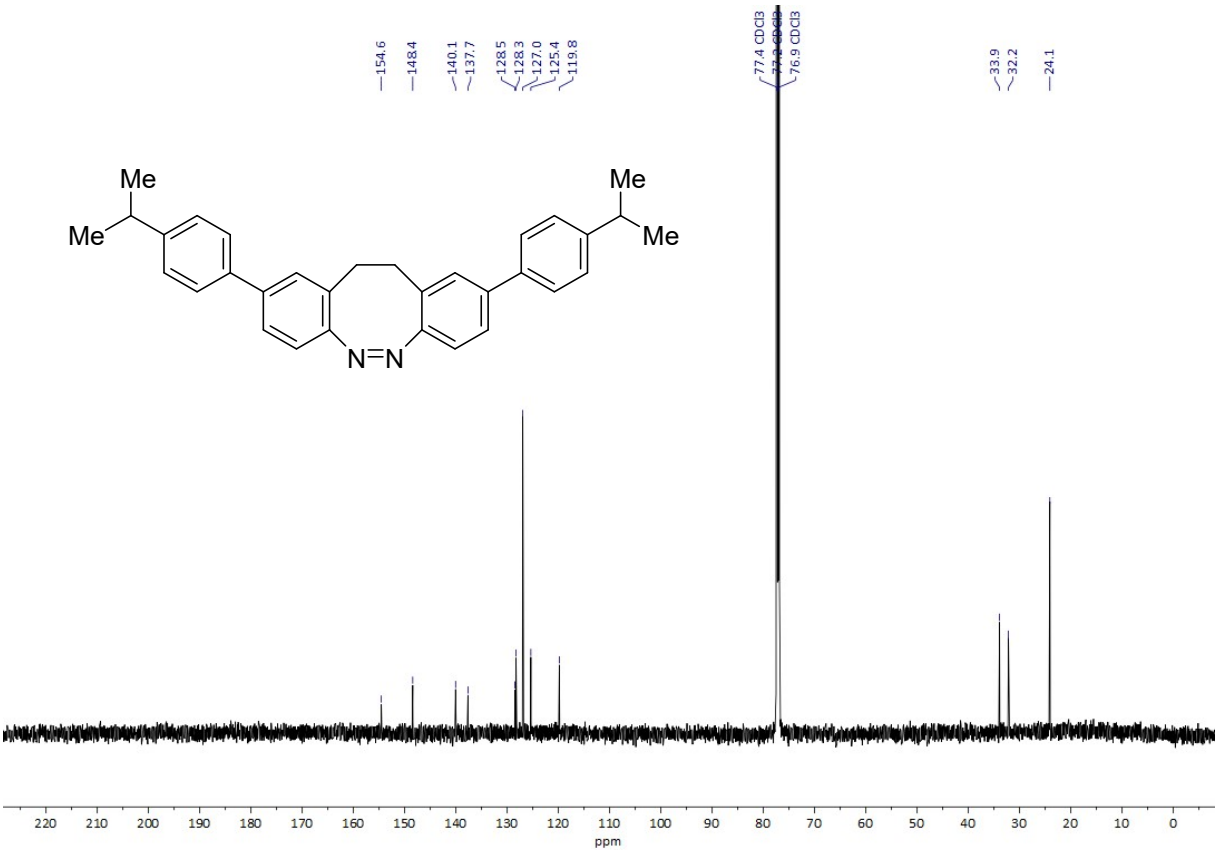


Figure 29: $^{13}C\{^{1}H\}$ NMR spectrum of **8** in $CDCl_3$.

(*Z*)-2,9-Bis(3-isopropylphenyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**9**)

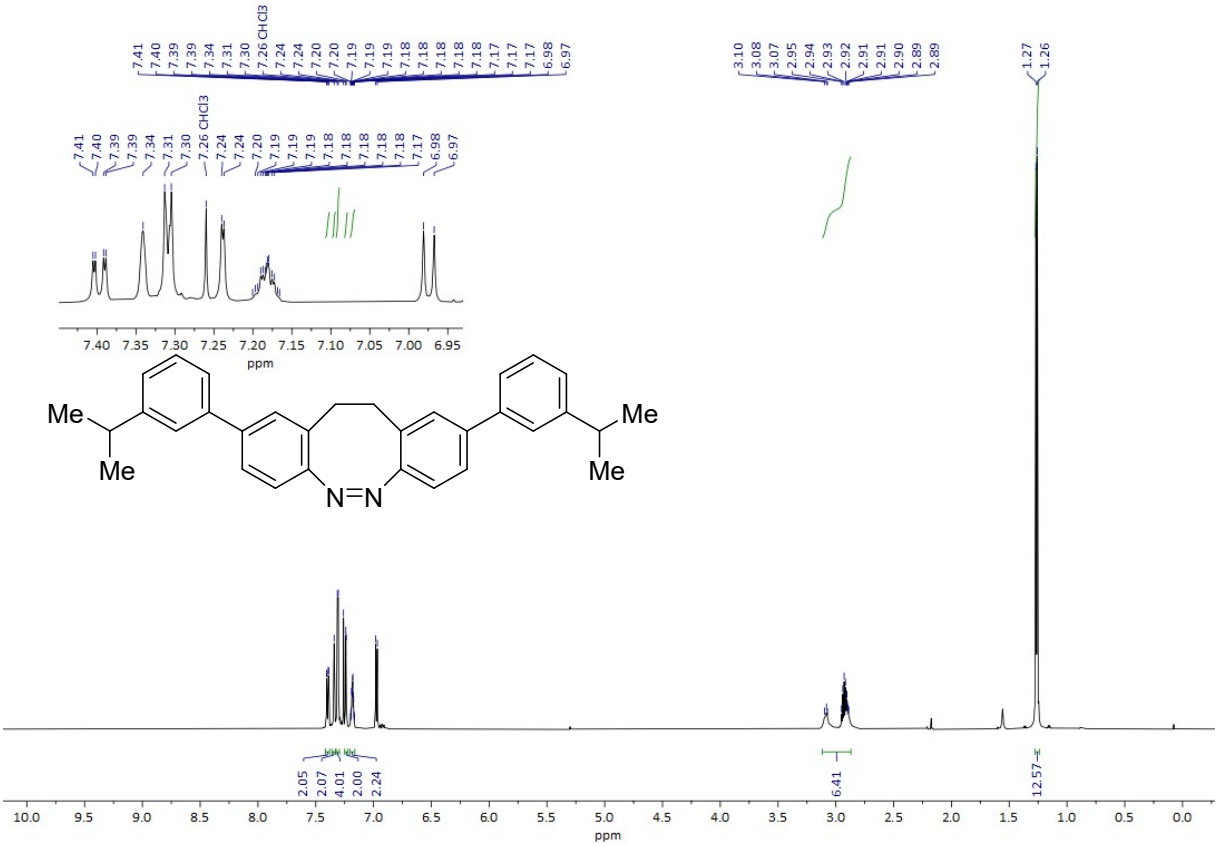


Figure 30: ^{1}H NMR spectrum of **9** in $CDCl_3$.

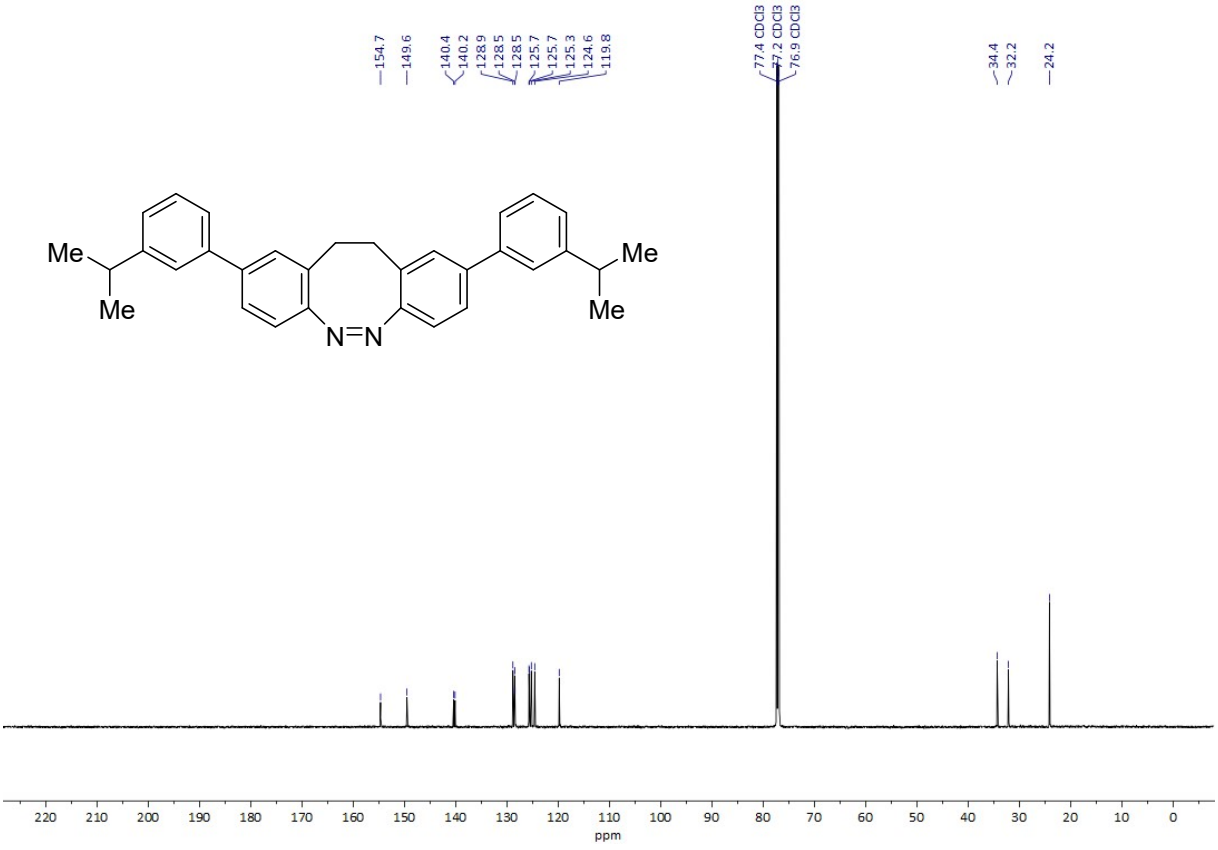


Figure 31: $^{13}C\{^{1}H\}$ NMR spectrum of **9** in $CDCl_3$.

(*Z*)-2,9-Bis(2-isopropylphenyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**10**)

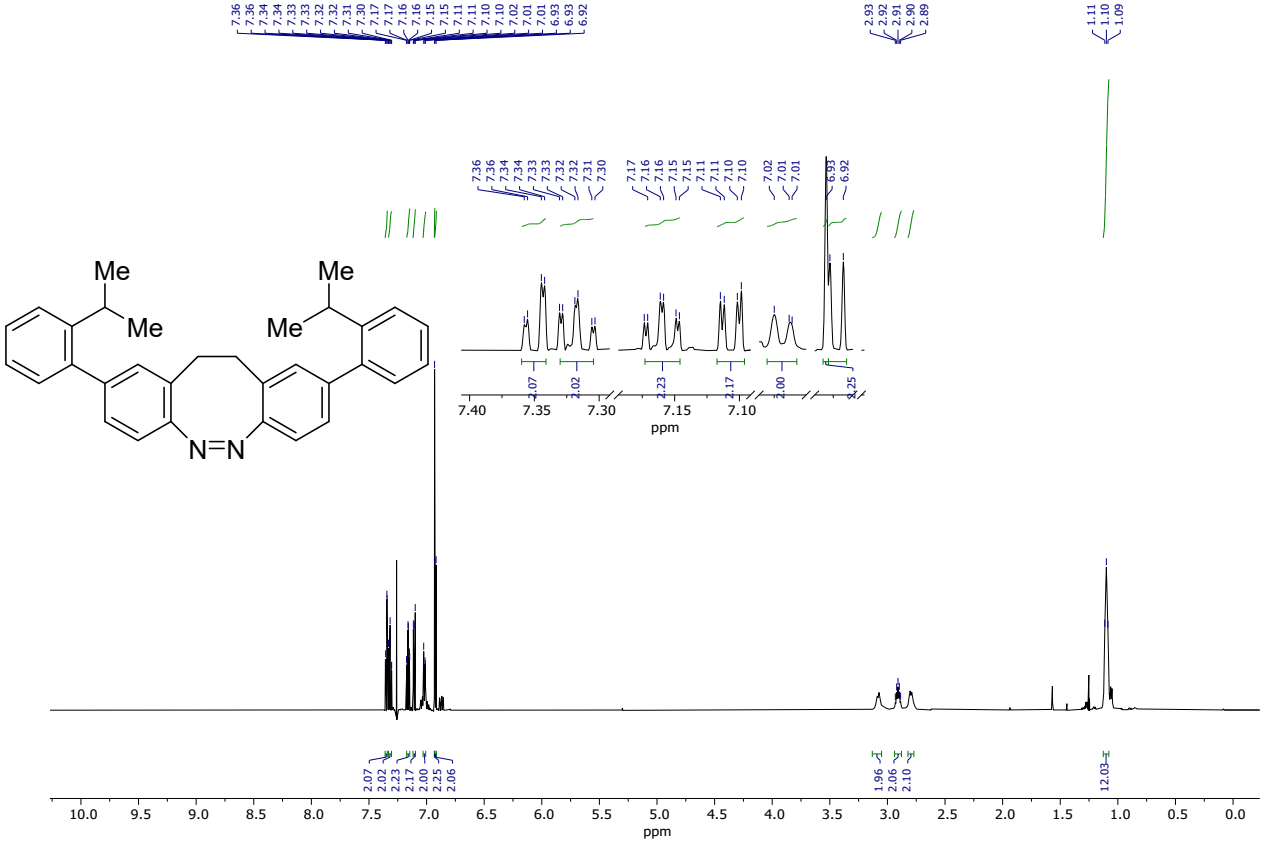


Figure 32: ^{1}H NMR spectrum of **10** in $CDCl_3$.

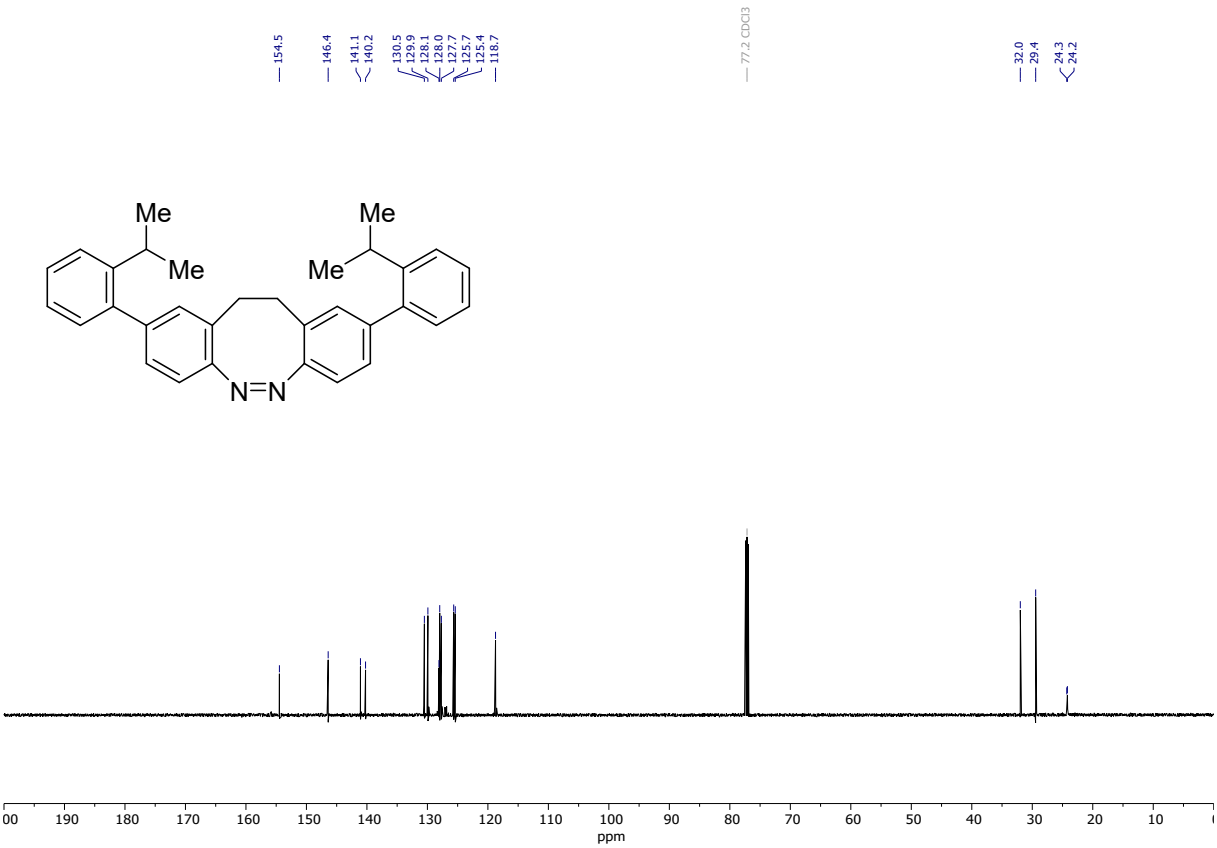


Figure 33: $^{13}C\{^{1}H\}$ NMR spectrum of **10** in $CDCl_3$.

(*Z*)-2,9-Dimesityl-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**11**)

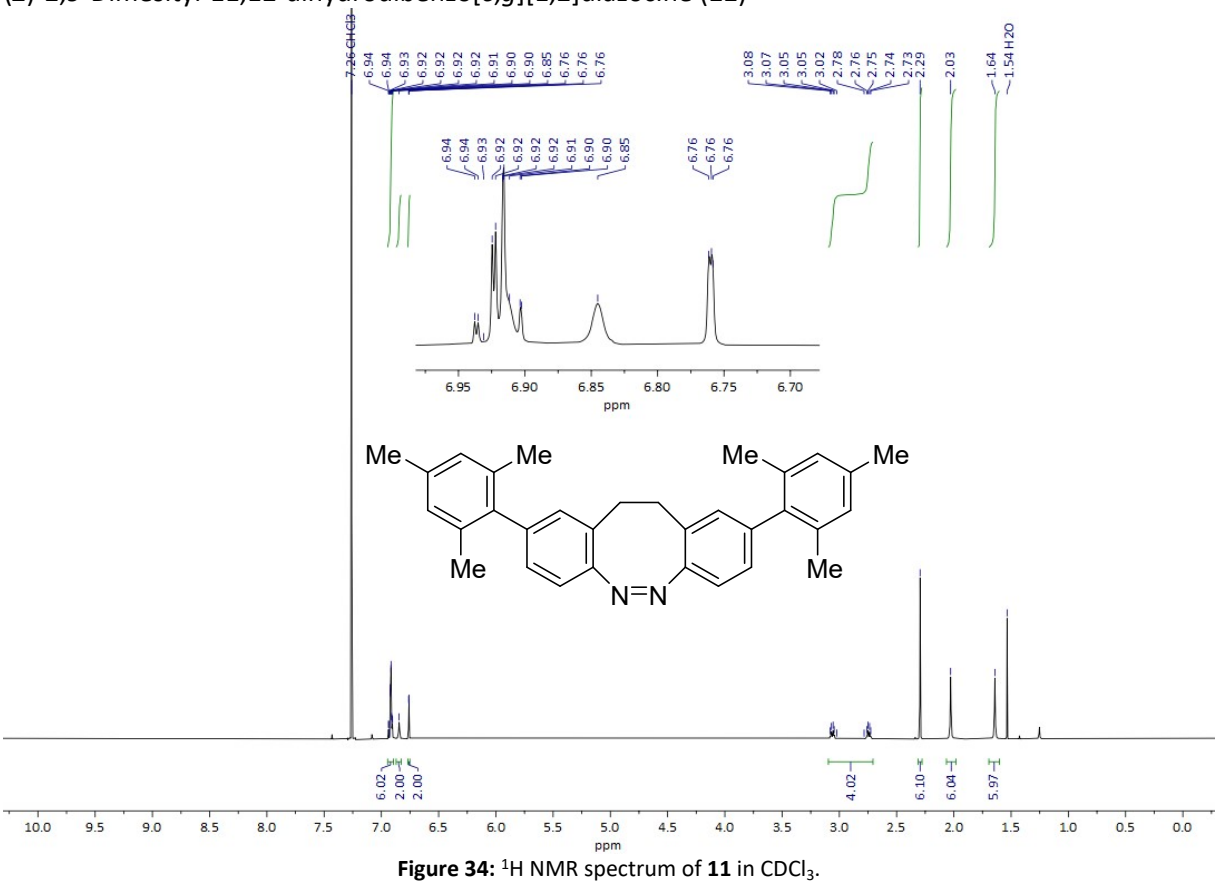


Figure 34: ^{1}H NMR spectrum of **11** in $CDCl_3$.

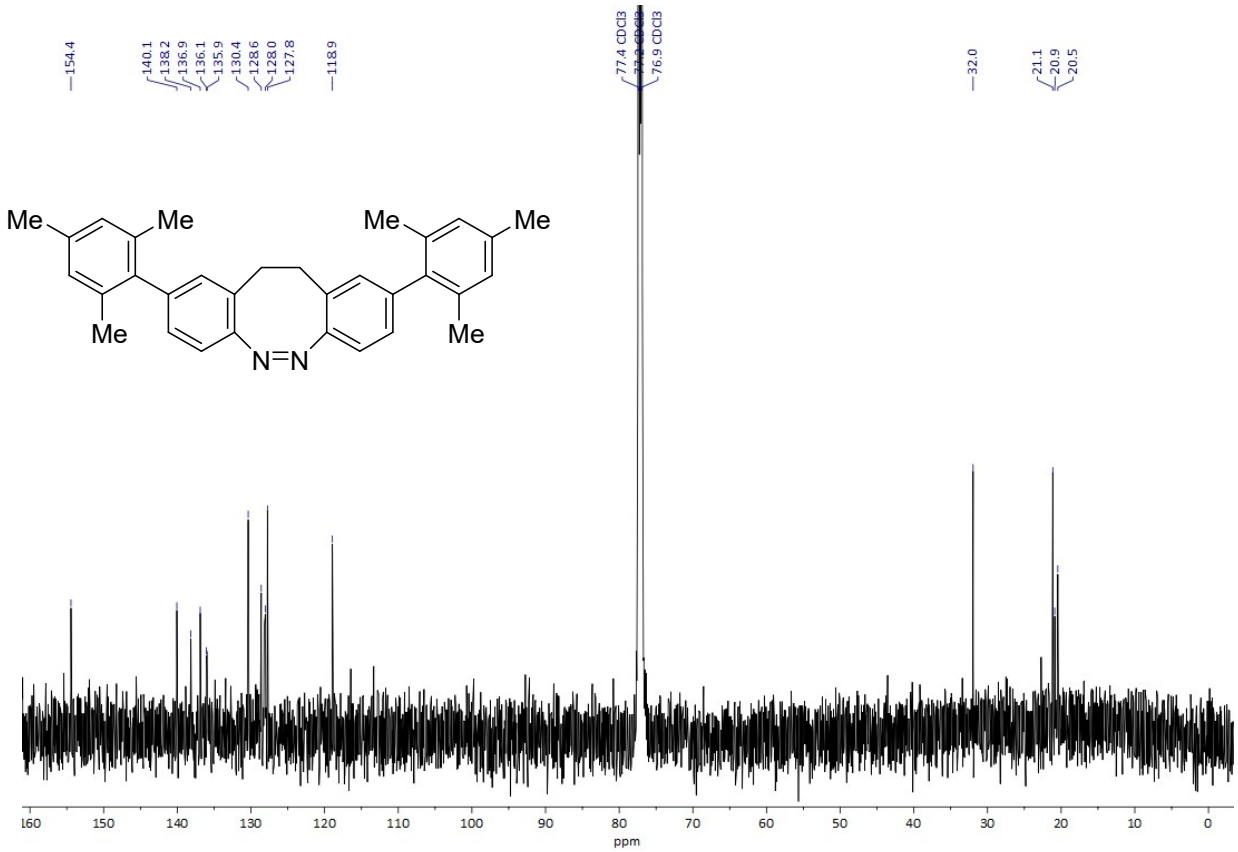


Figure 35: $^{13}C\{^{1}H\}$ NMR spectrum of **11** in $CDCl_3$.

(*Z*)-2,9-Bis(4-methoxyphenyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**12**)

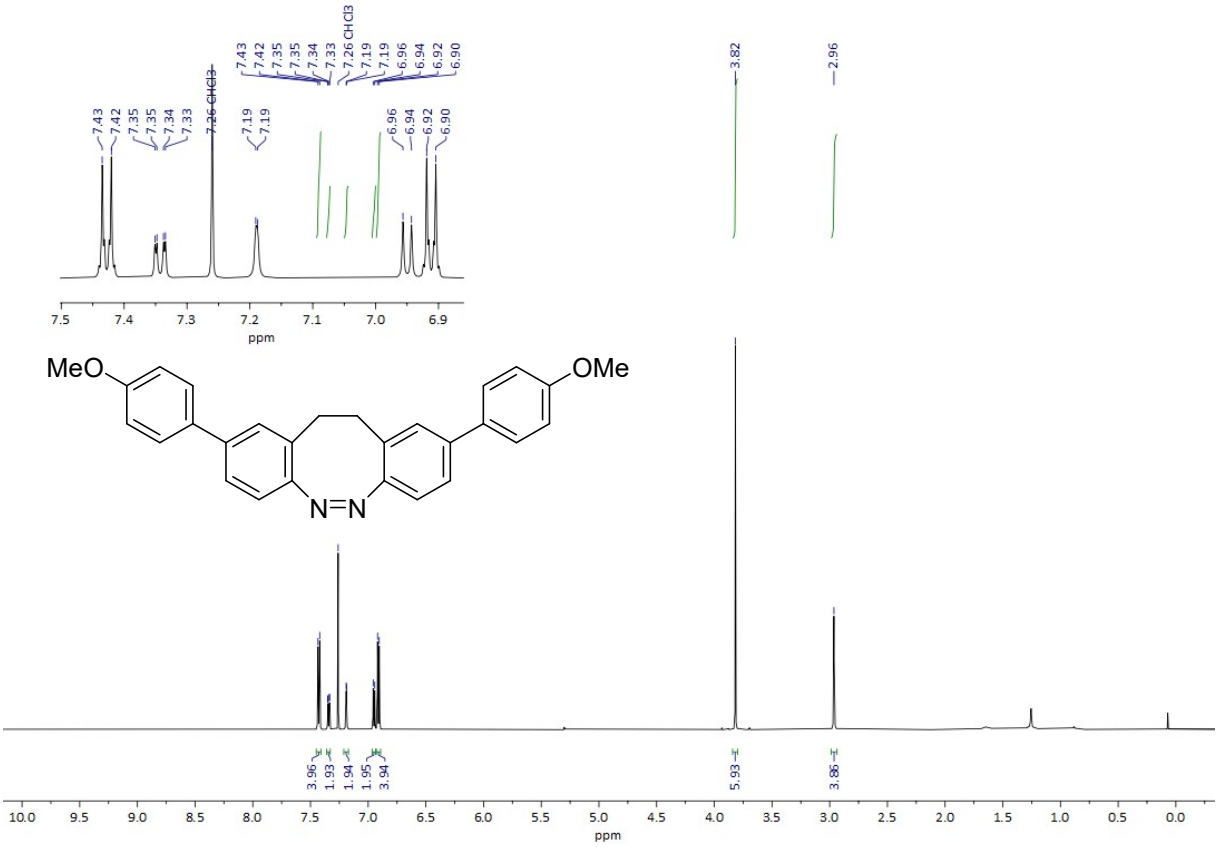


Figure 36: ^{1}H NMR spectrum of **12** in $CDCl_3$.

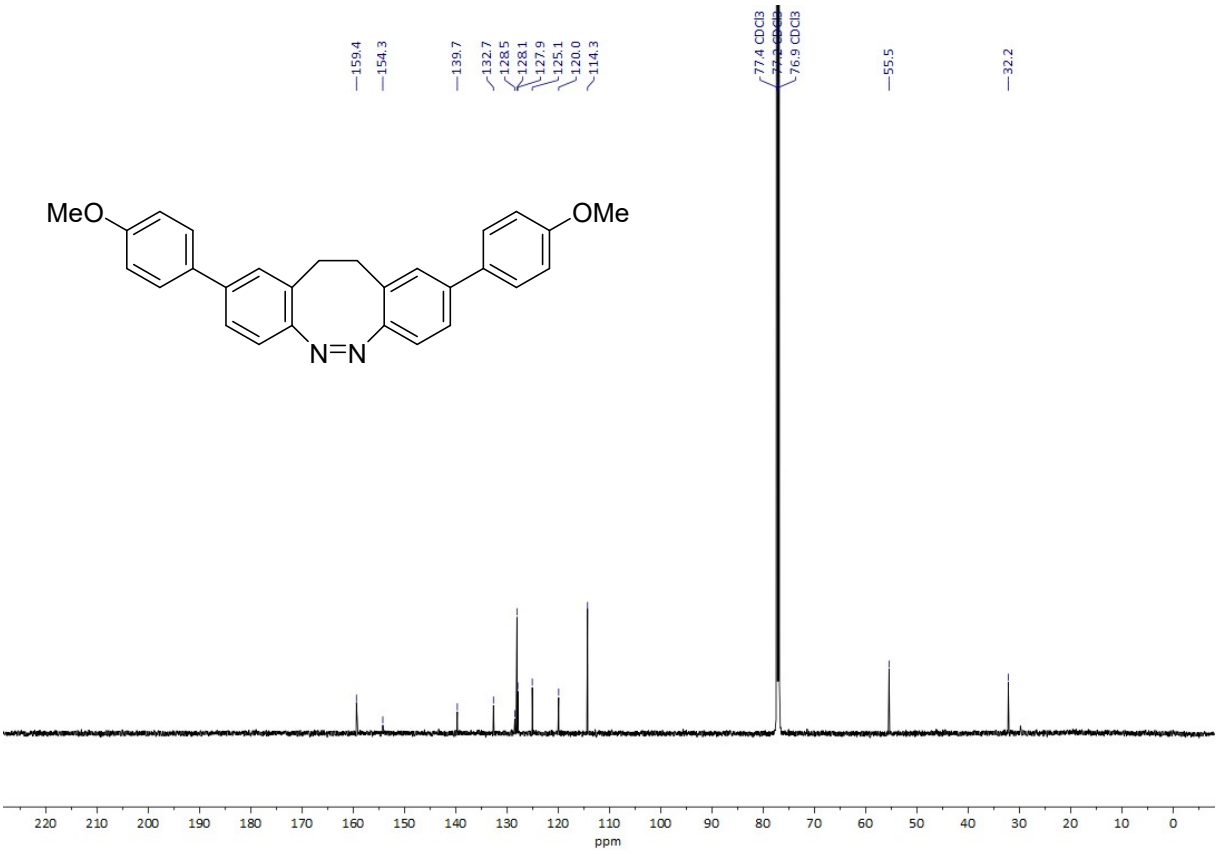


Figure 37: $^{13}C\{^{1}H\}$ NMR spectrum of **12** in $CDCl_3$.

(*Z*)-4,4'-(11,12-Dihydrodibenzo[*c*,*g*][1,2]diazocine-2,9-diyl)diphenol (**13**)

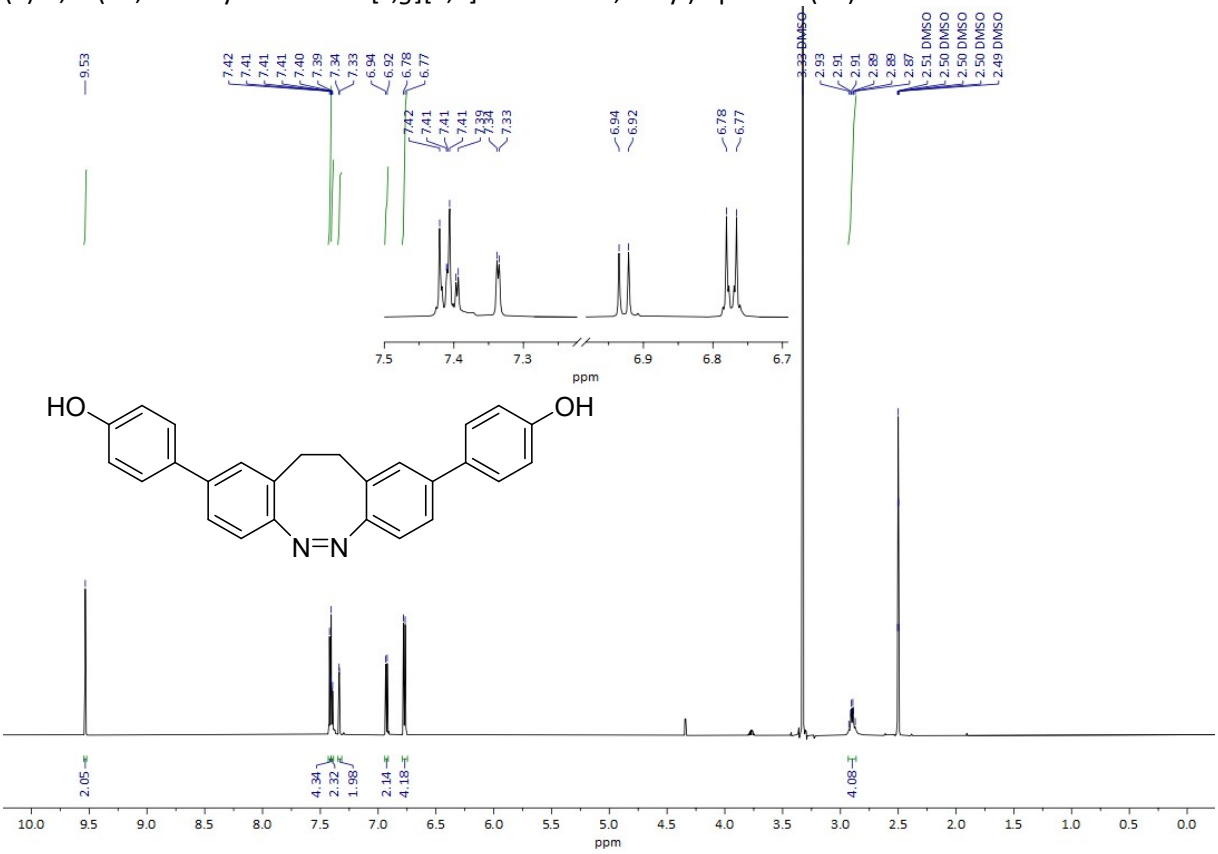


Figure 38: ^{1}H NMR spectrum of **13** in DMSO-d_6.

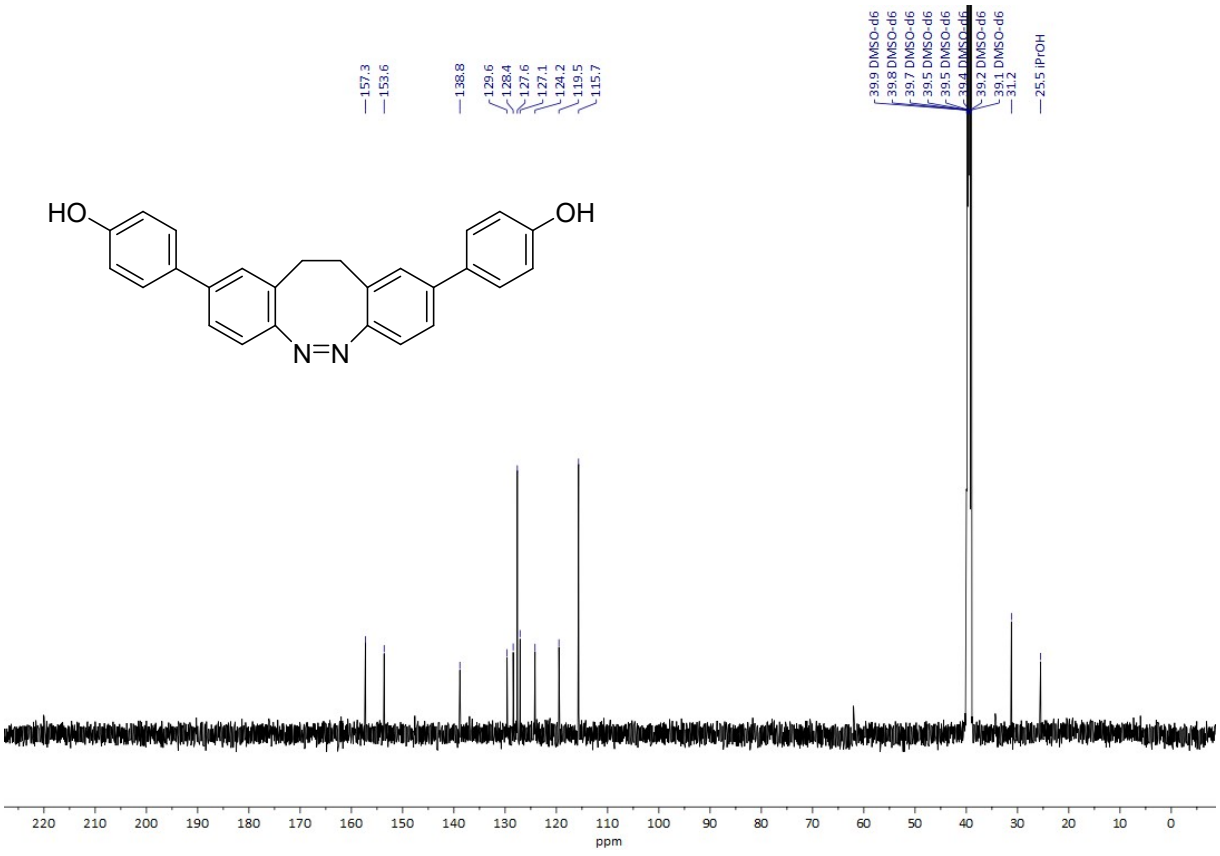


Figure 39: $^{13}C\{^{1}H\}$ NMR spectrum of **13** in DMSO-d_6.

(Z)-4-(11,12-Dihydrodiben-zo[*c,g*][1,2]diazocin-2-yl)phenol (**32**)

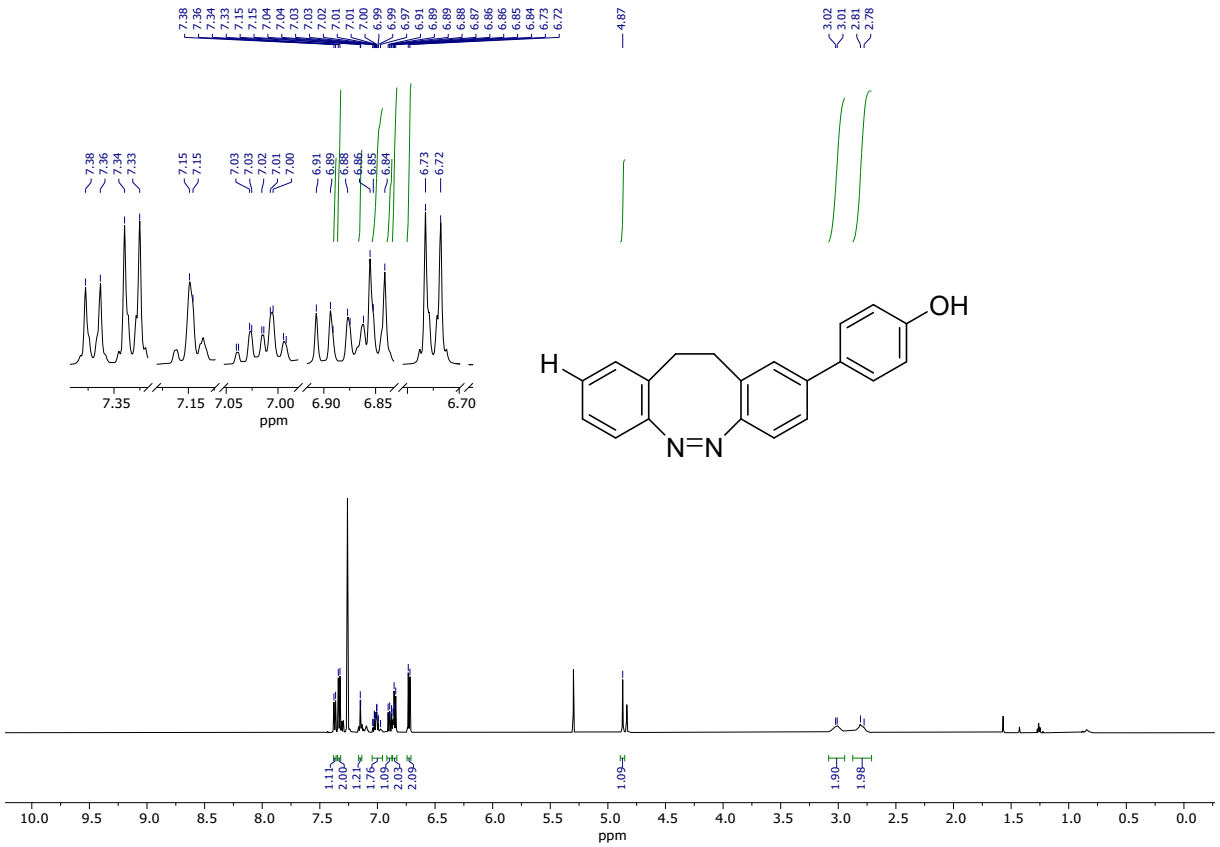


Figure 40*:* ^{1}H NMR spectrum of **32** in $CDCl_3$.

(*Z*)-4,4'-(11,12-Dihydrodibenzo[*c*,*g*][1,2]diazocine-2,9-diyl)bis(N,N-dimethylaniline)-diazocine (**14**)

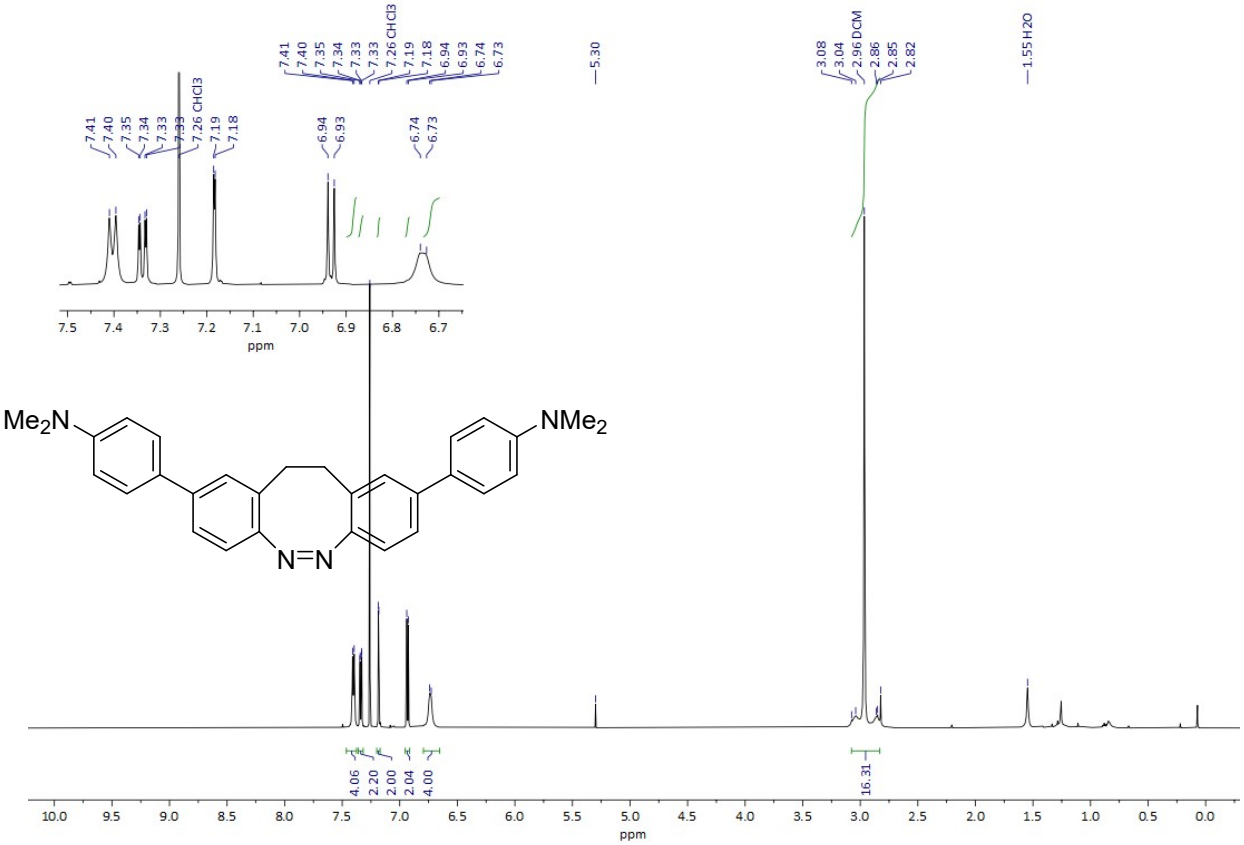


Figure 41: ^{1}H NMR spectrum of **14** in $CDCl_3$.

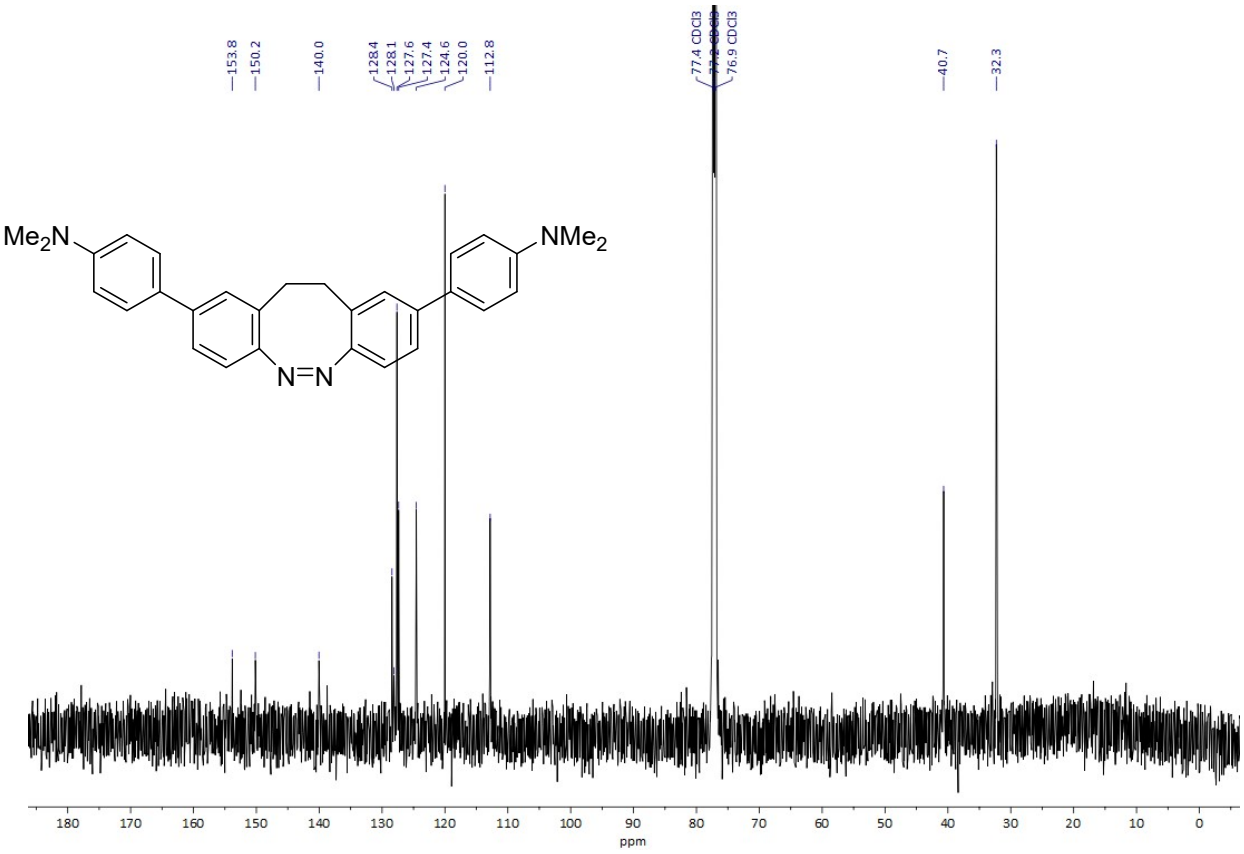


Figure 42: $^{13}C\{^{1}H\}$ NMR spectrum of **14** in $CDCl_3$.

(*Z*)-4,4'-(11,12-Dihydrodibenzo[*c*,*g*][1,2]diazocine-2,9-diyl)bis(*N*,*N*-diphenylaniline) (**15**)

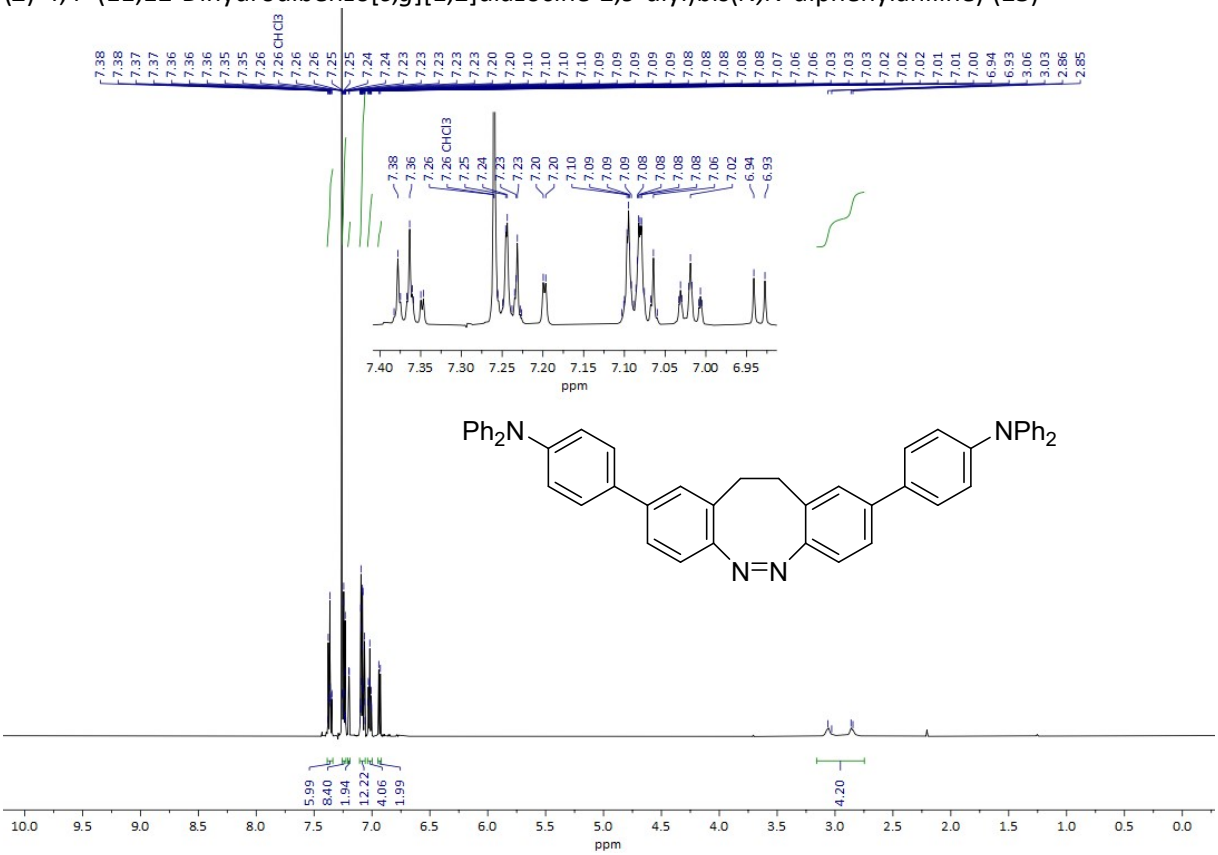


Figure 43: ^{1}H NMR spectrum of **15** in $CDCl_3$.

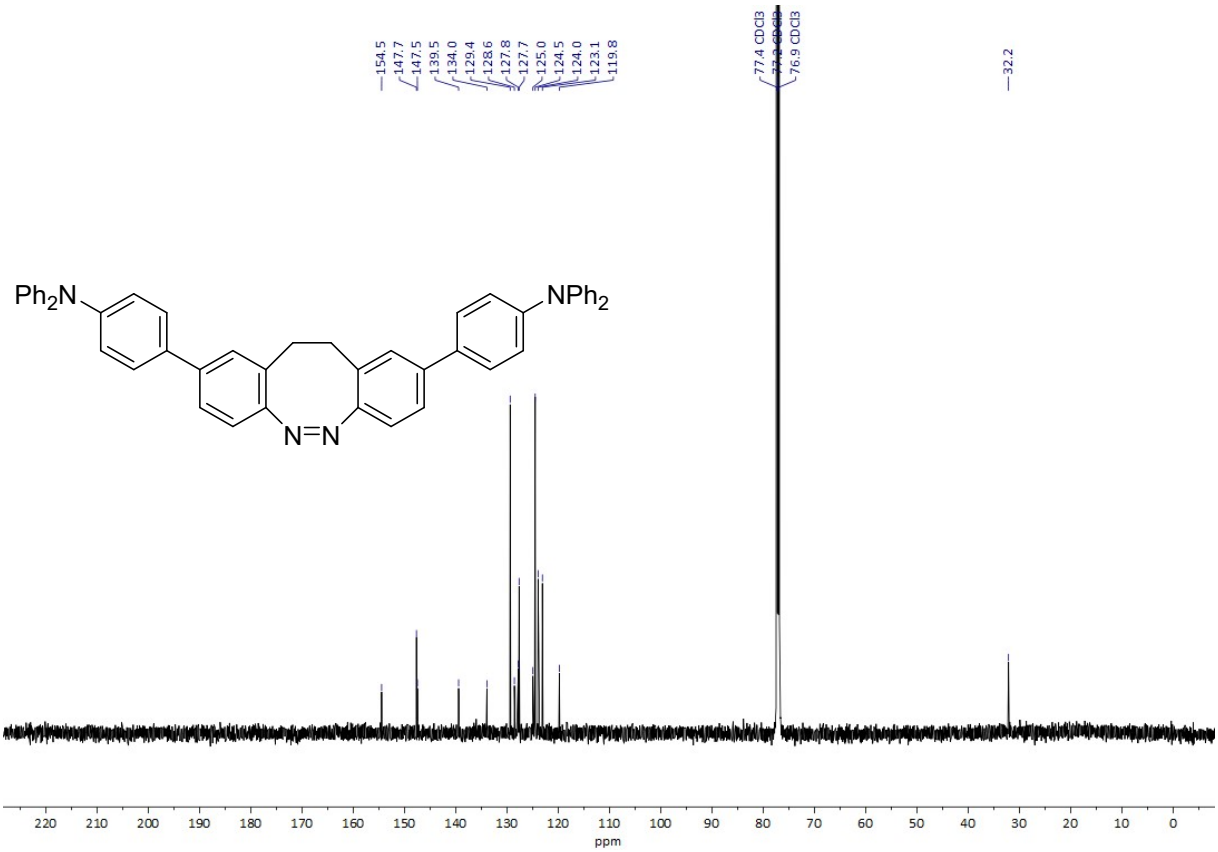


Figure 44: $^{13}C\{^{1}H\}$ NMR spectrum of **15** in $CDCl_3$.

(*Z*)-4,4'-(11,12-Dihydrodibenzo[*c*,*g*][1,2]diazocine-2,9-diyl)dianiline (**16**)

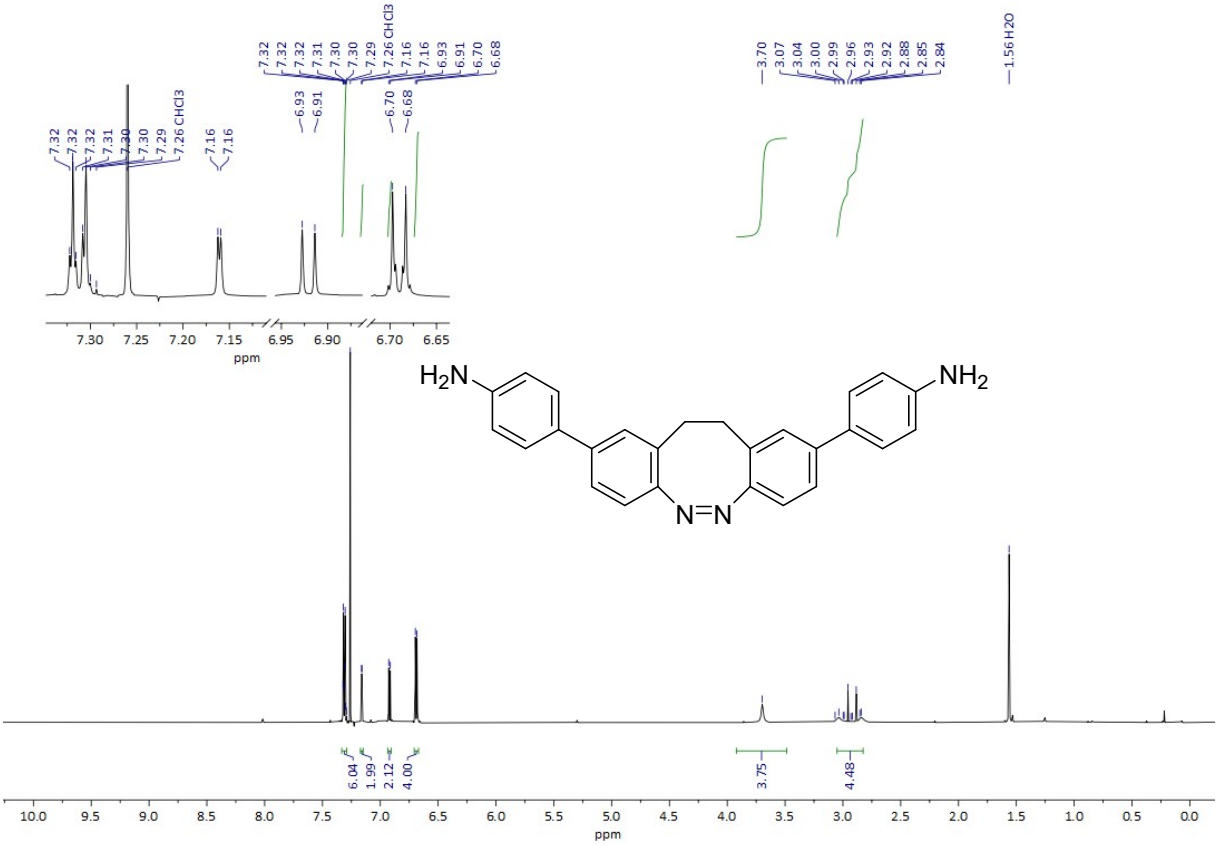


Figure 45: ^{1}H NMR spectrum of **16** in $CDCl_3$.

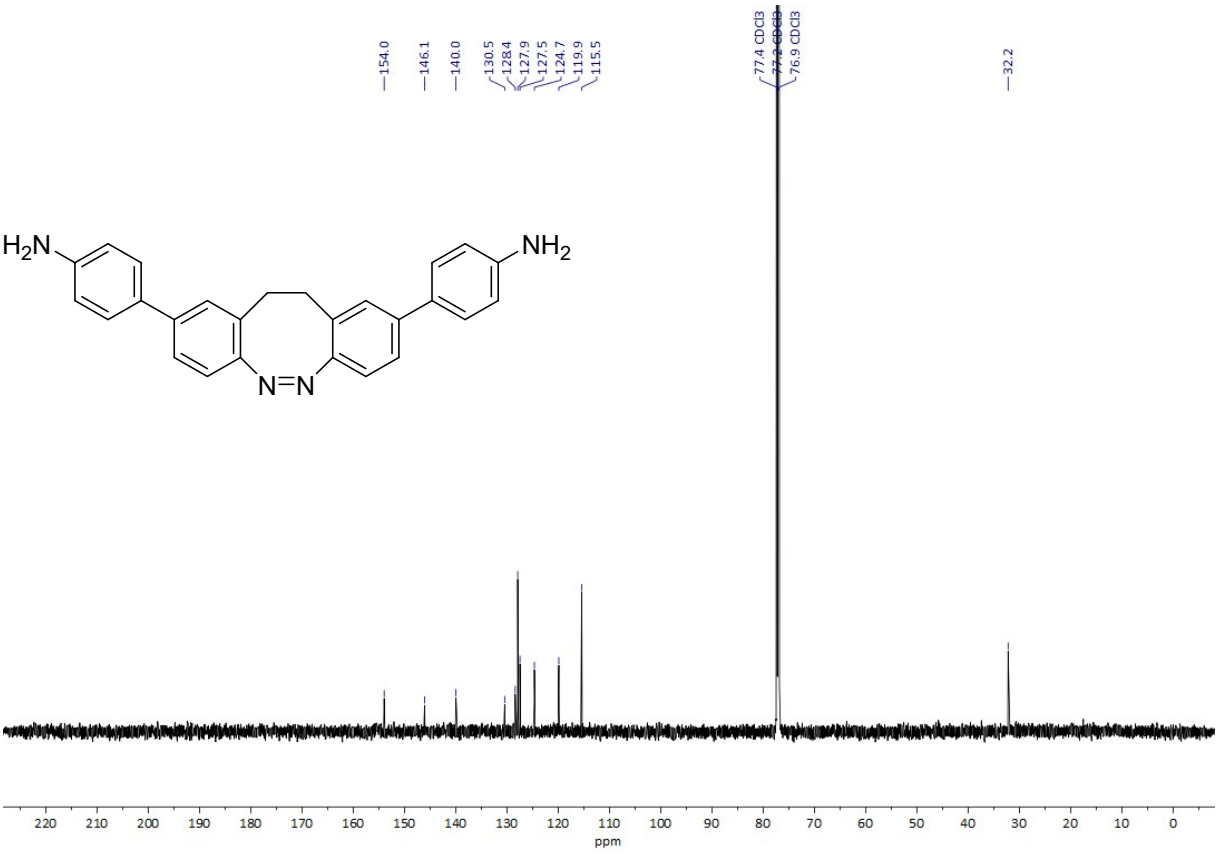


Figure 46: $^{13}C\{^{1}H\}$ NMR spectrum of **16** in $CDCl_3$.

(*Z*)-4-(11,12-Dihydrodiben-zo[*c*,*g*][1,2]diazocin-2-yl)aniline (**33**)

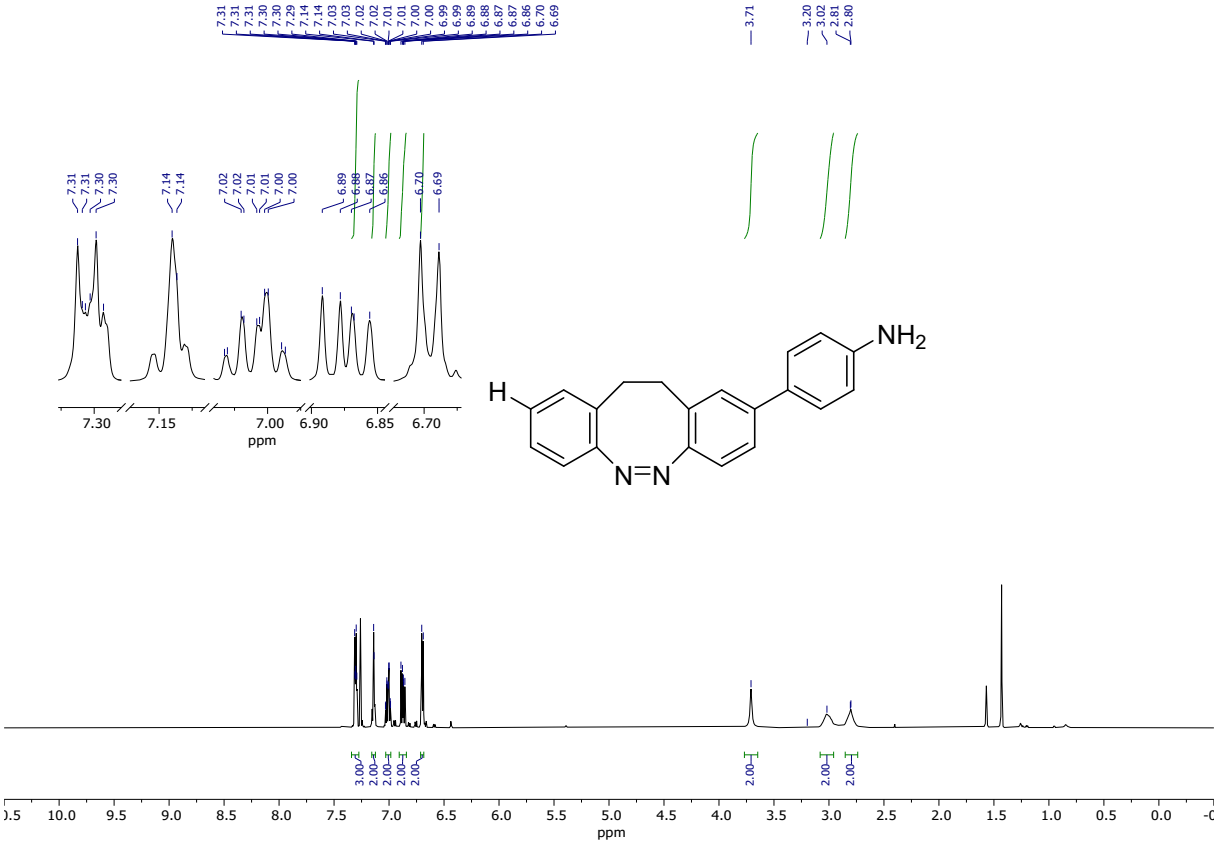


Figure 47: ^{1}H NMR spectrum of **33** in $CDCl_3$.

(*Z*)-*N*1-(4-(11,12-Dihydrodi-benzo[*c*,*g*][1,2]diazocin-2-yl)phenyl)benzene-1,4-diamine (**34**)

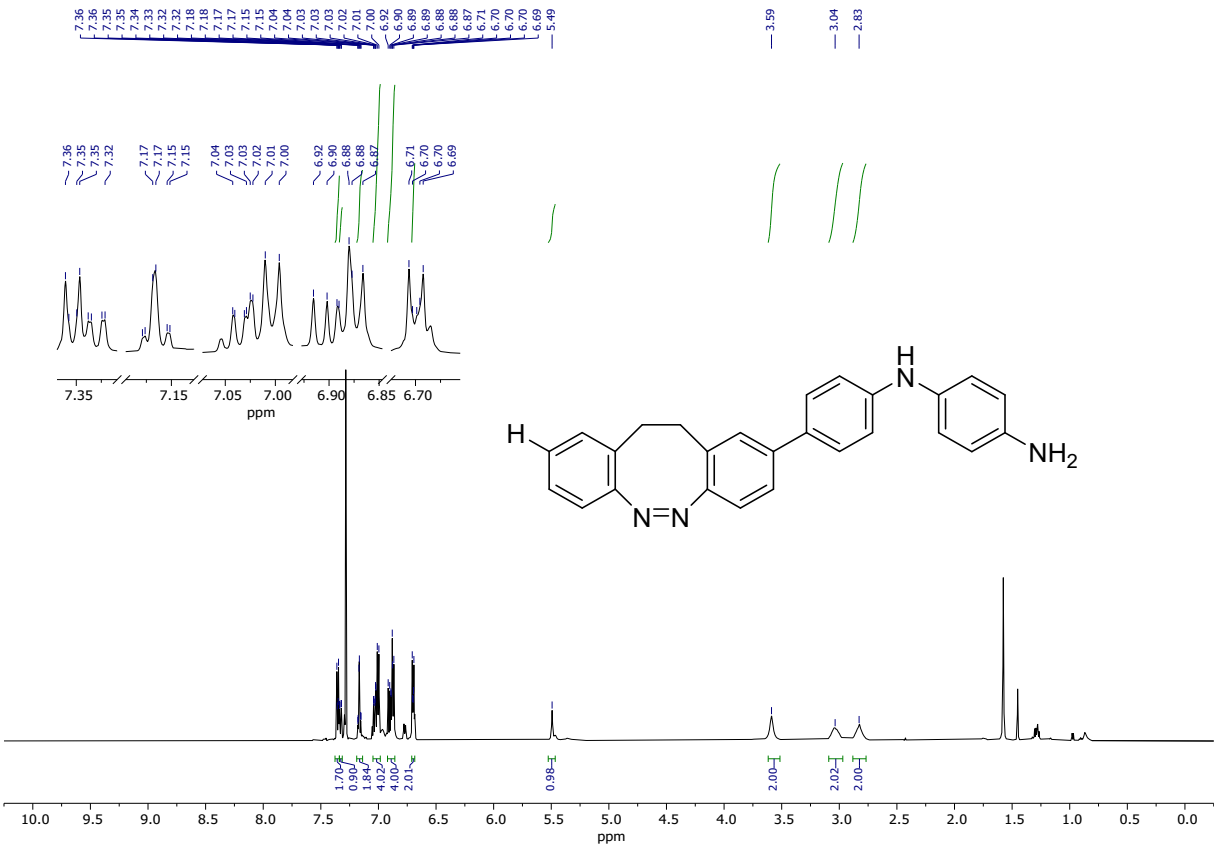


Figure 48: ^{1}H NMR spectrum of **34** in $CDCl_3$.

(*Z*)-2,9-Bis(4-nitrophenyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**17**)

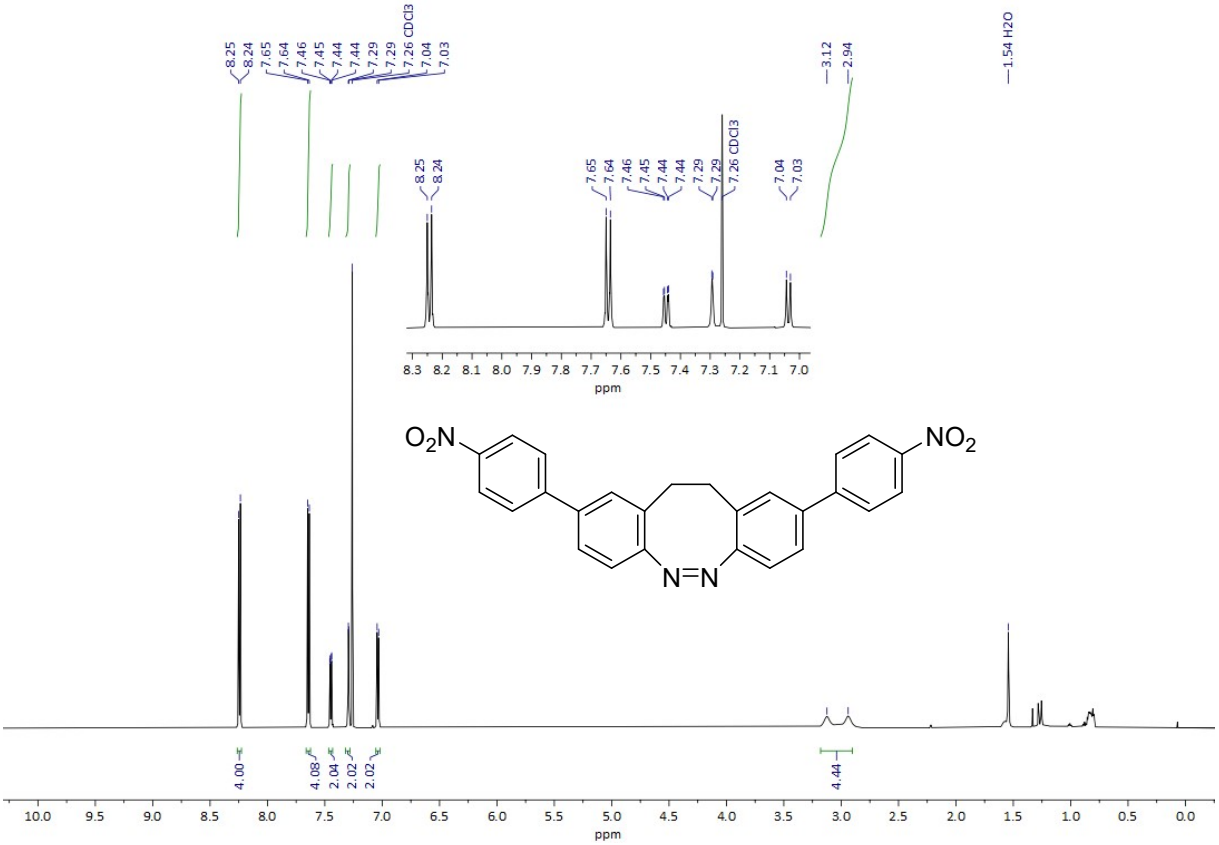


Figure 52: ^{1}H NMR spectrum of **17** in $CDCl_3$.

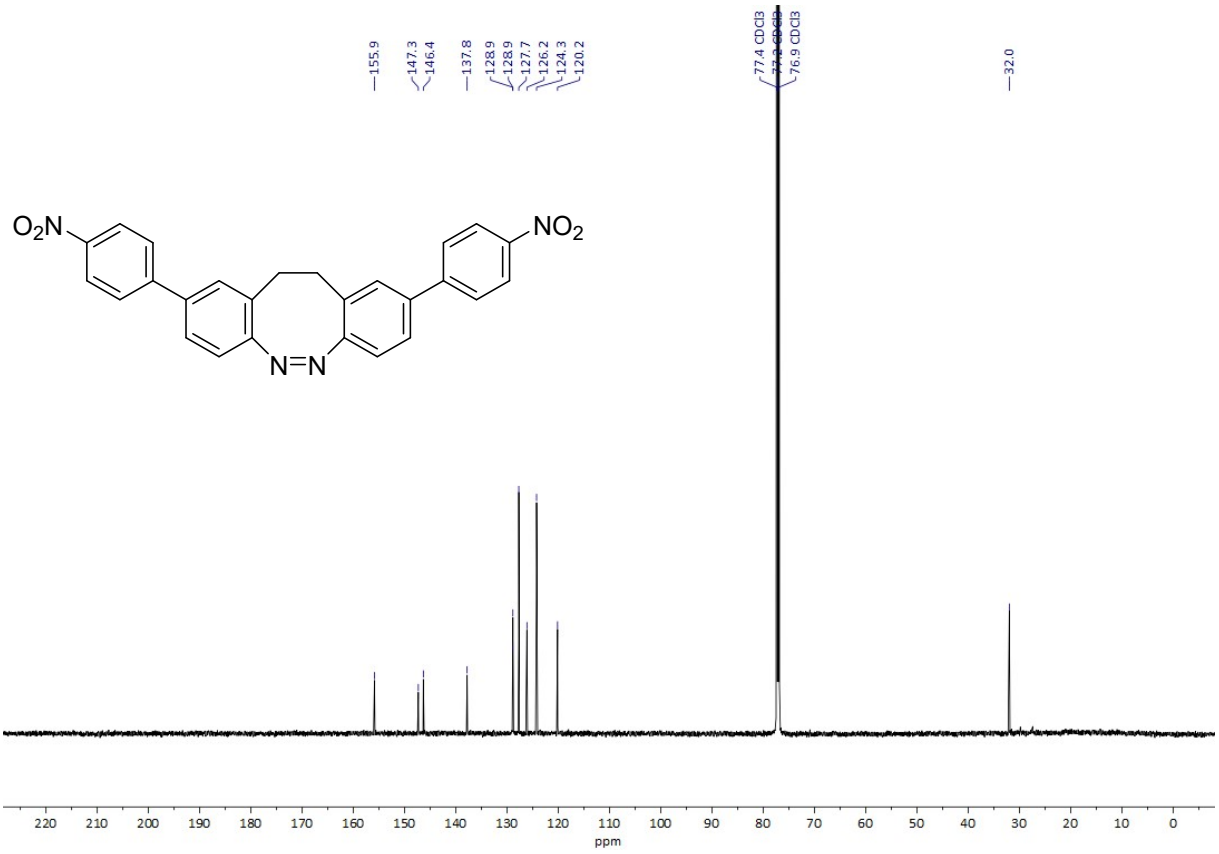


Figure 53: $^{13}C\{^{1}H\}$ NMR spectrum of **17** in $CDCl_3$.

(*Z*)-2,9-Bis(3-nitrophenyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**18**)

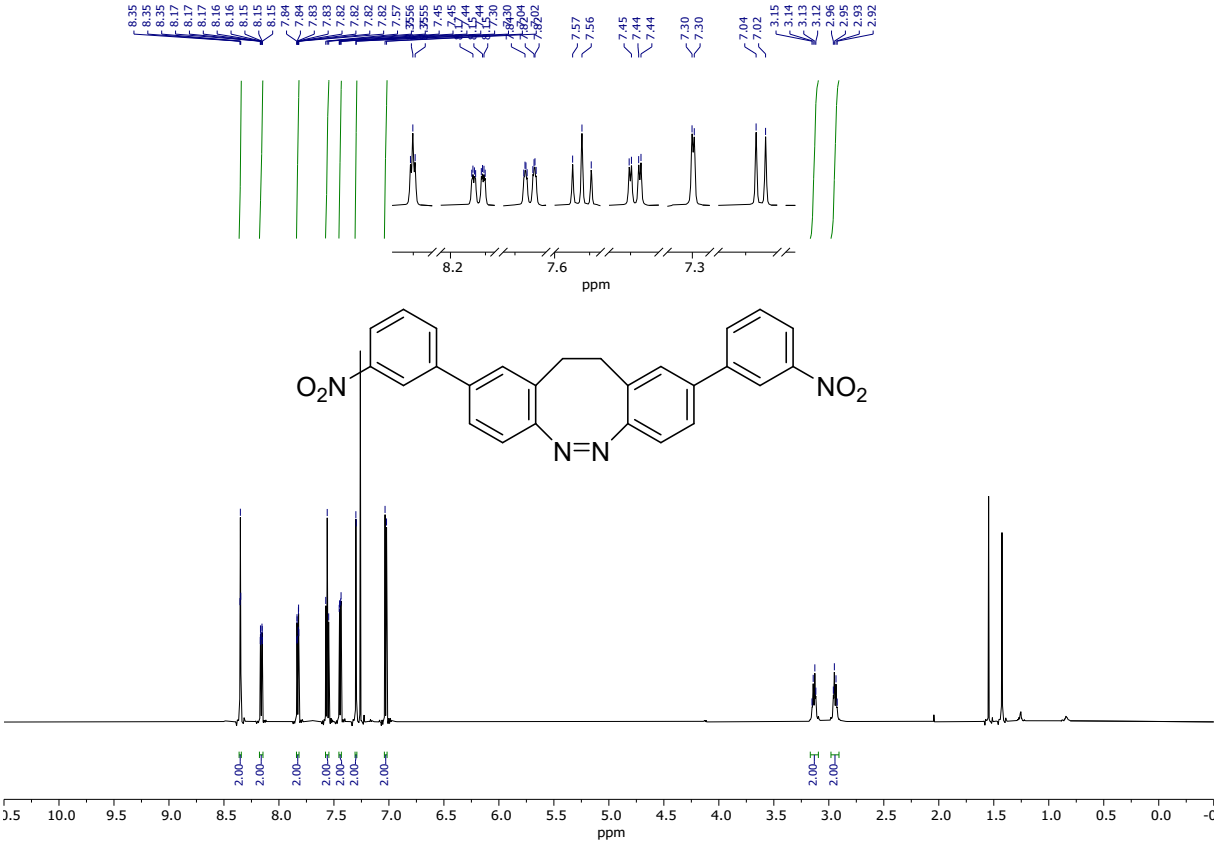


Figure 54: ^{1}H NMR spectrum of **18** in $CDCl_3$.

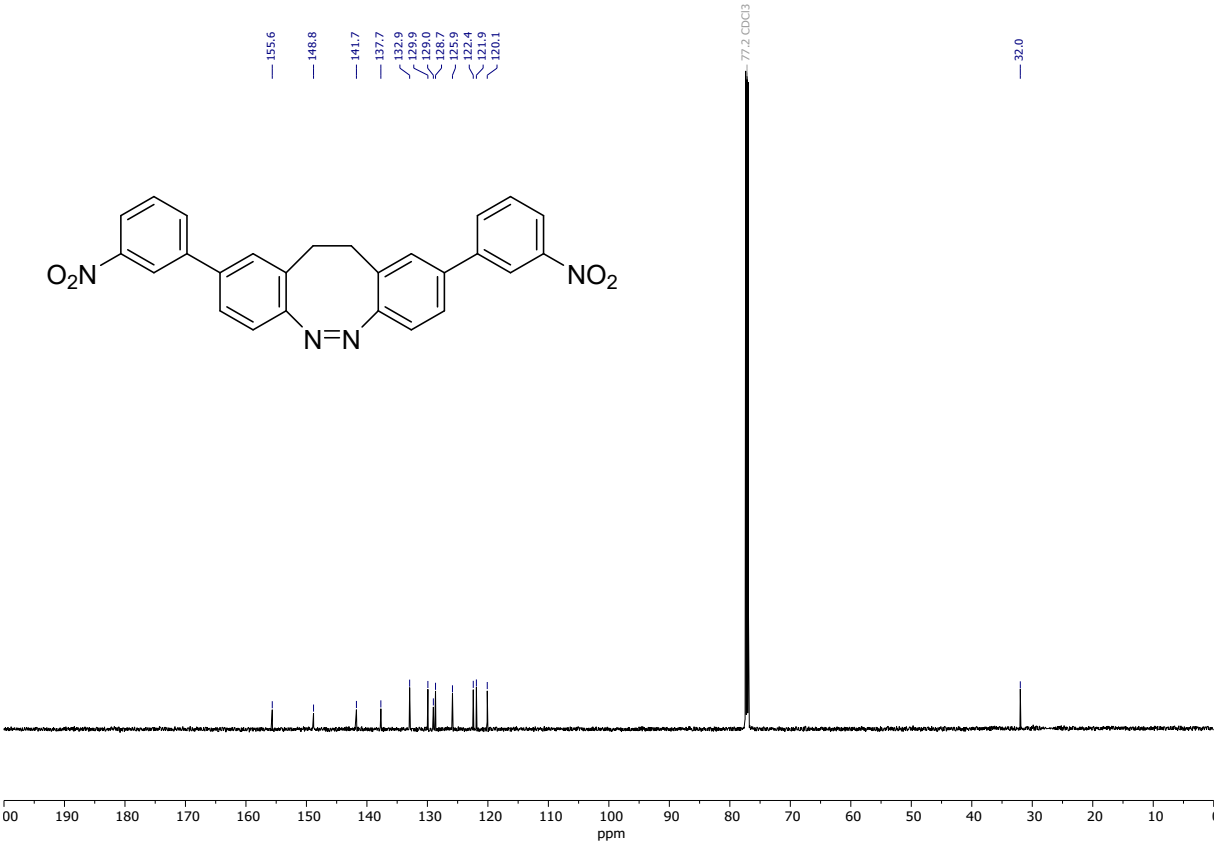


Figure 55: $^{13}C\{^{1}H\}$ NMR spectrum of **18** in $CDCl_3$.

(*Z*)-2,9-Bis(2-nitrophenyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**19**)

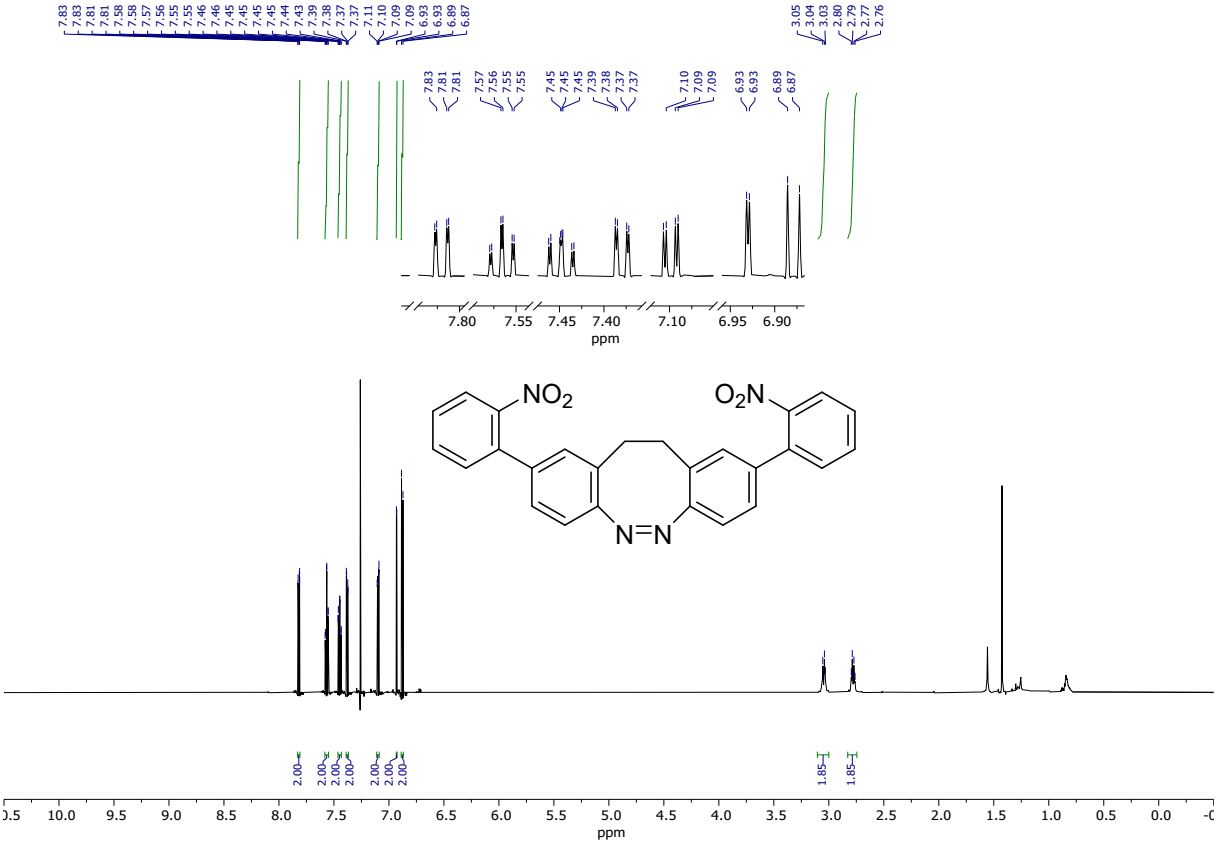


Figure 56: ^{1}H NMR spectrum of **19** in $CDCl_3$.

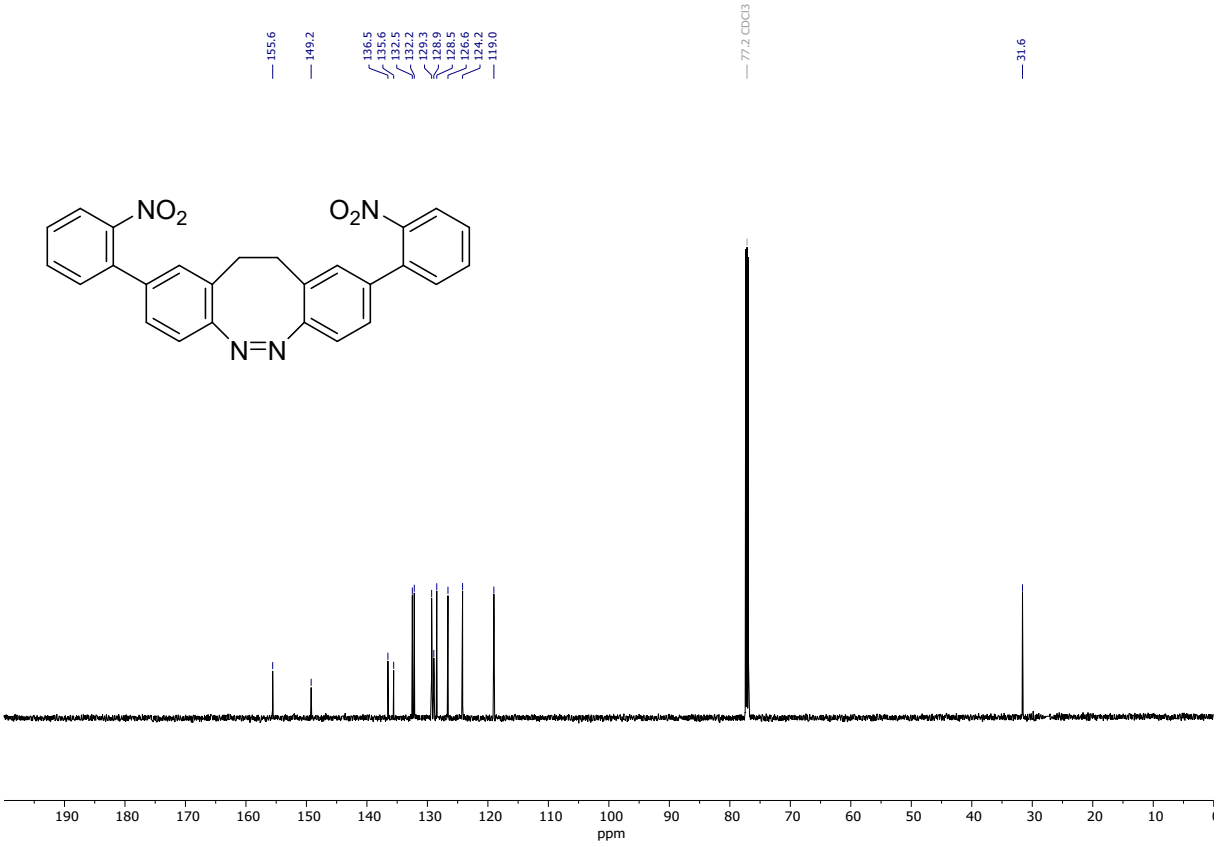


Figure 57: $^{13}C\{^{1}H\}$ NMR spectrum of **19** in $CDCl_3$.

(*Z*)-2,9-Bis(3,5-bis(trifluoromethyl)phenyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**20**)

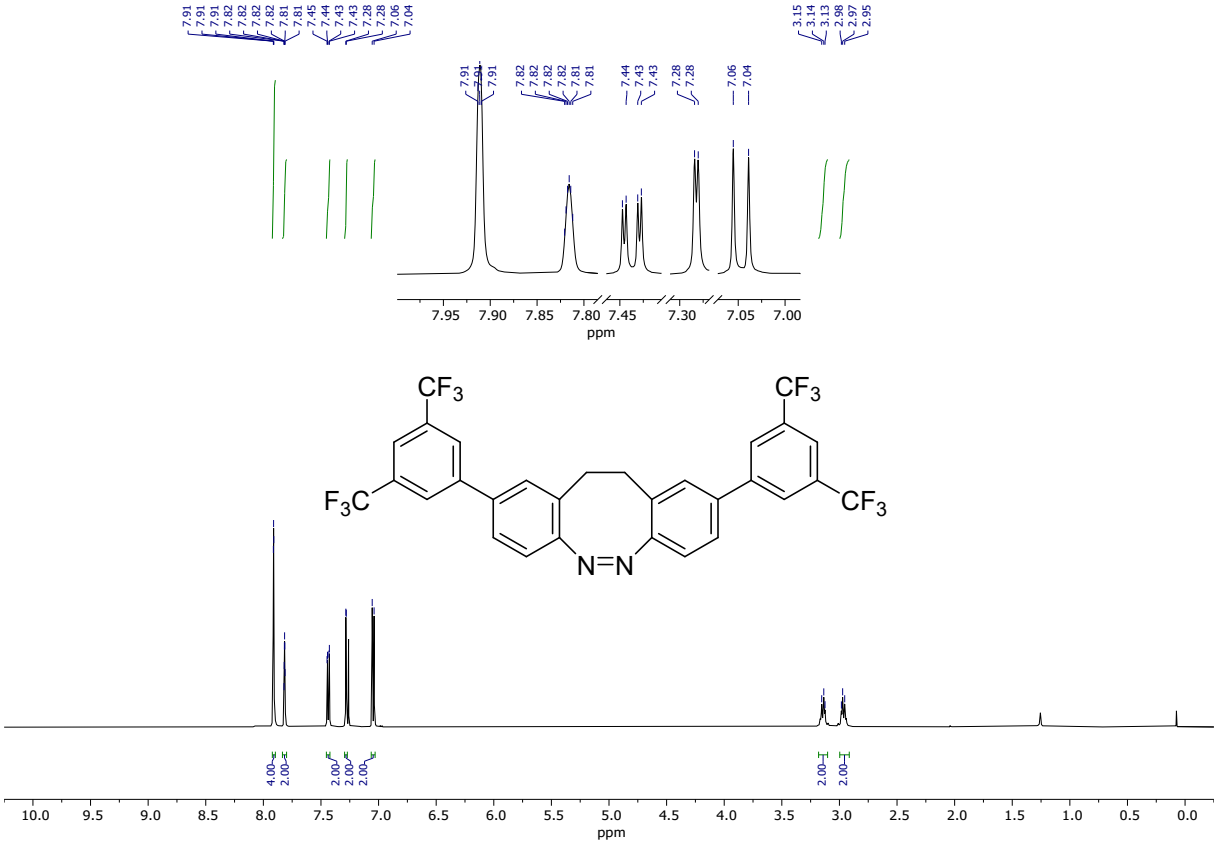


Figure 49: ^{1}H NMR spectrum of **20** in $CDCl_3$.

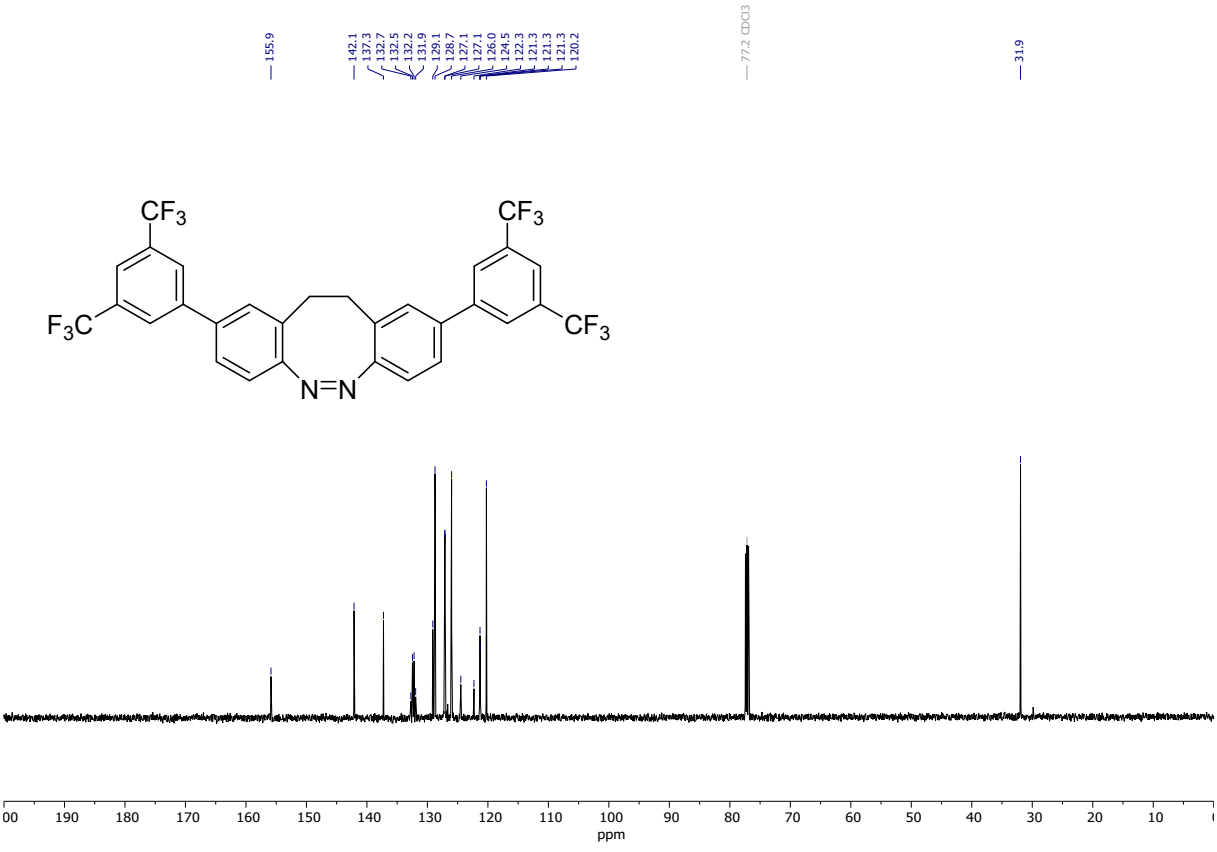


Figure 50: $^{13}C\{^{1}H\}$ NMR spectrum of **20** in $CDCl_3$.

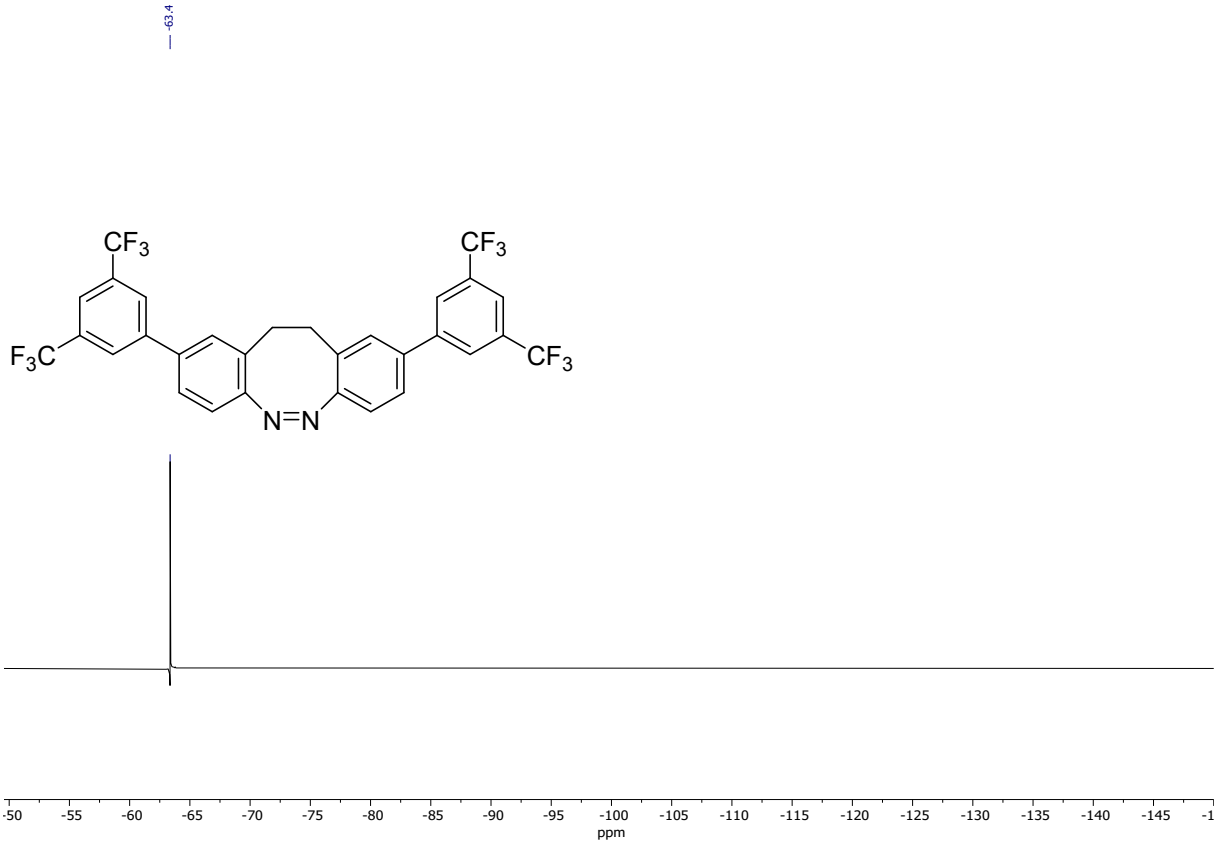


Figure 51: $^{19}F\{^{1}H\}$ NMR spectrum of **20** in $CDCl_3$.

(*Z*)-4,4'-(11,12-Dihydrodibenzo[*c*,*g*][1,2]diazocine-2,9-diyl)dibenzonitrile (**21**)

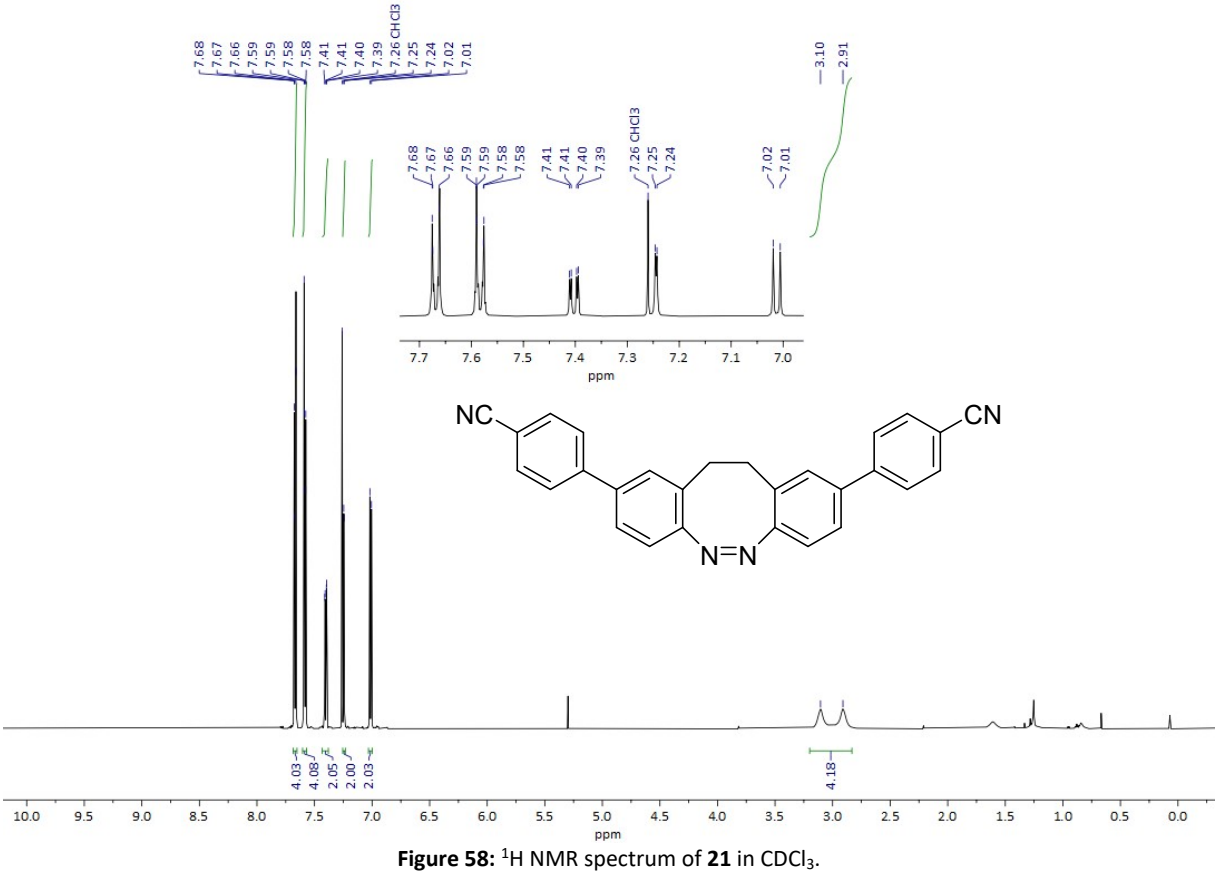


Figure 58: ^{1}H NMR spectrum of **21** in $CDCl_3$.

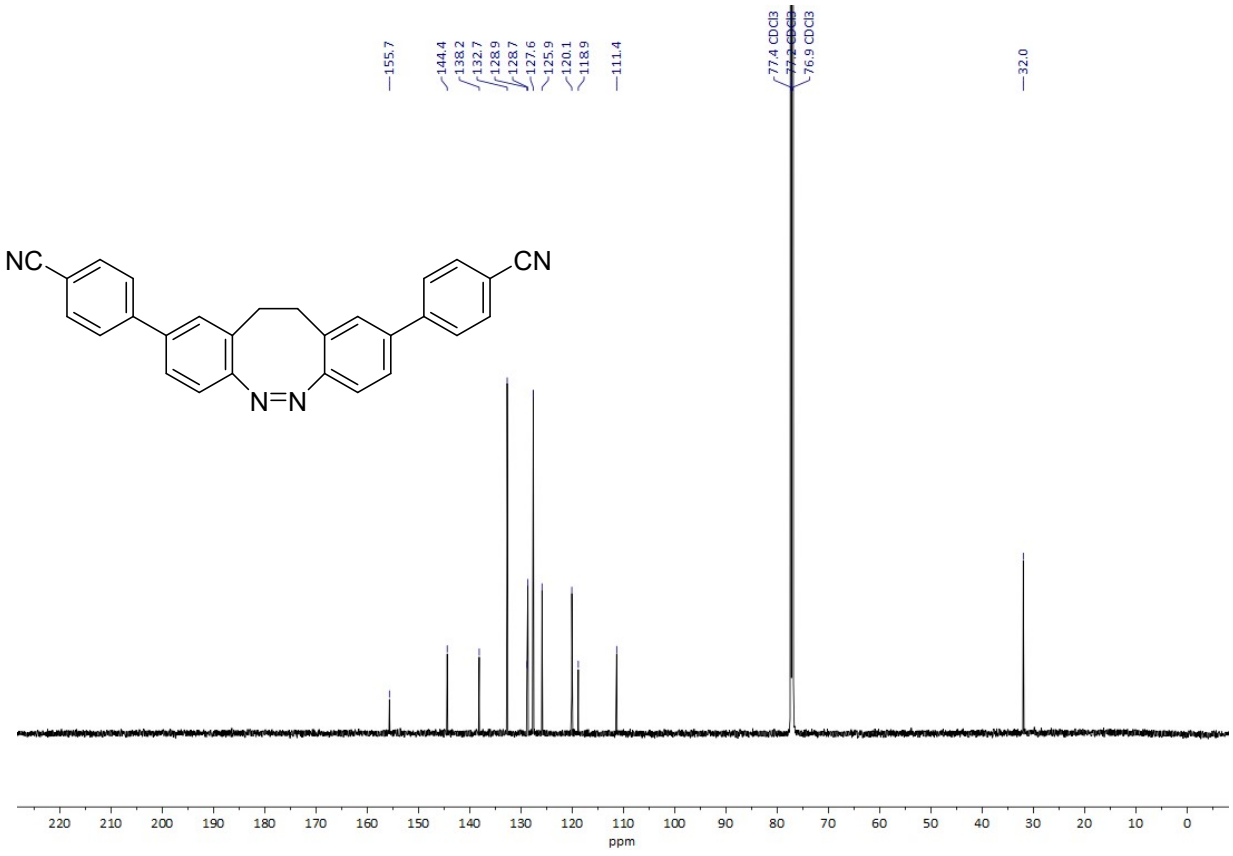


Figure 59: $^{13}C\{^{1}H\}$ NMR spectrum of **21** in $CDCl_3$.

(*Z*)-1,1'-((11,12-Dihydrodibenzo[*c*,*g*][1,2]diazocine-2,9-diyl)bis(4,1-phenylene))bis-(ethan-1-one) (**22**)

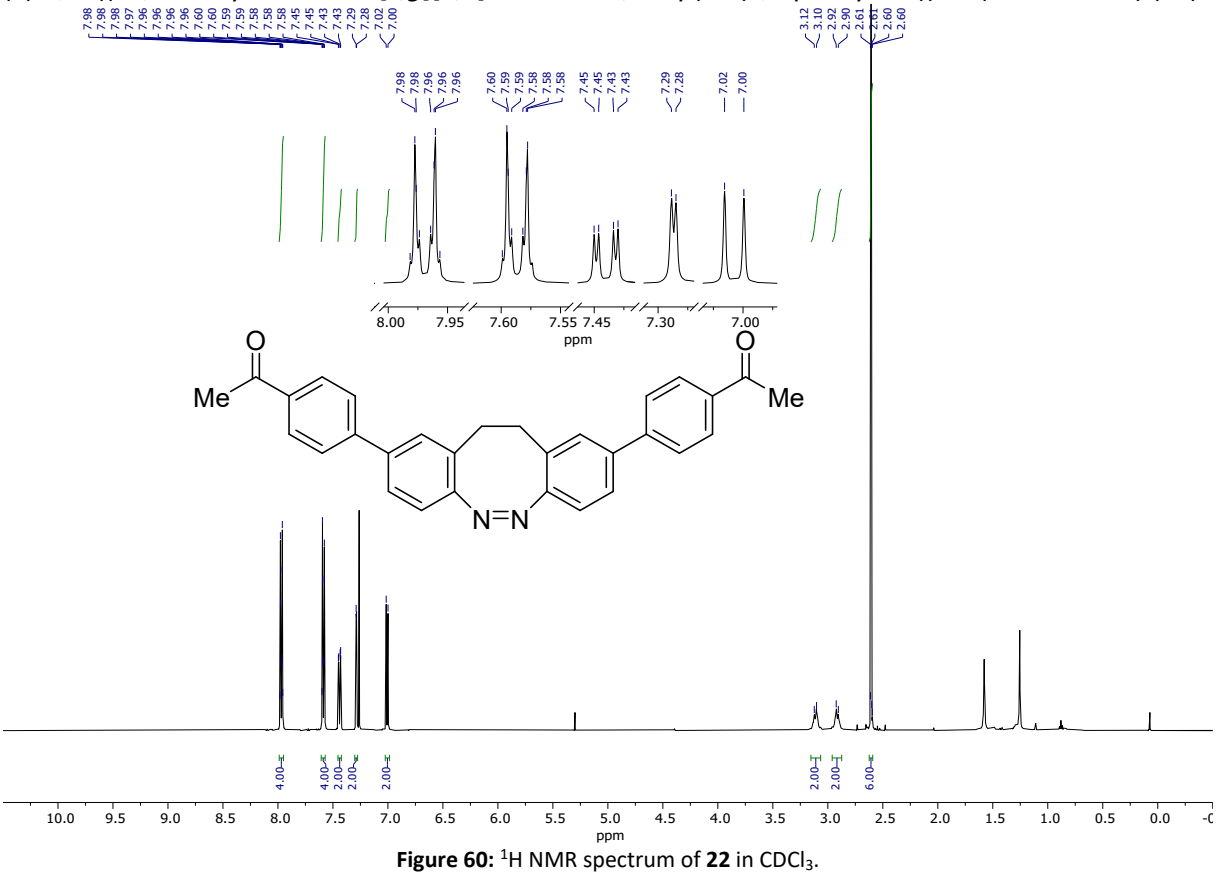


Figure 60: ^{1}H NMR spectrum of **22** in $CDCl_3$.

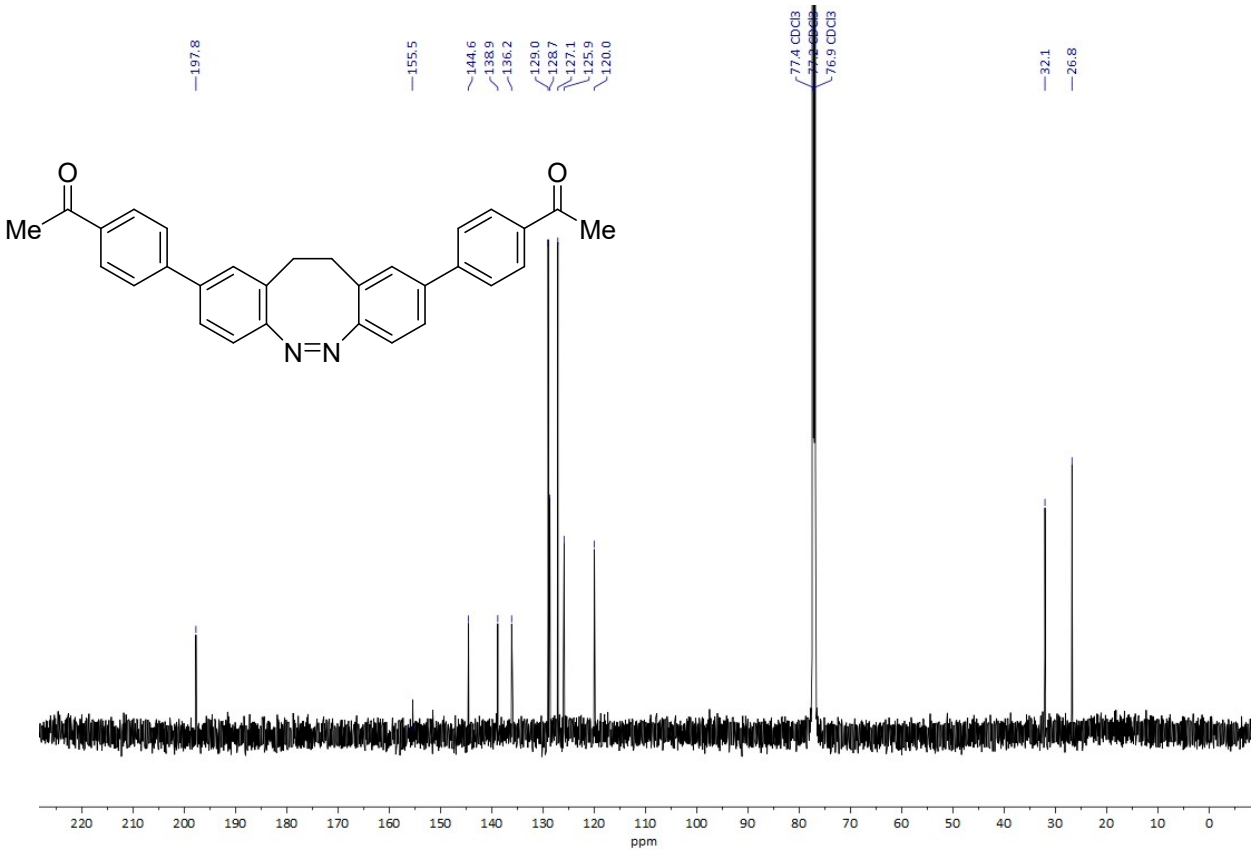


Figure 61: $^{13}C\{^{1}H\}$ NMR spectrum of **22** in $CDCl_3$.

Dimethyl 4,4'-(11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine-2,9-diyl)(*Z*)-dibenzoate (**23**)

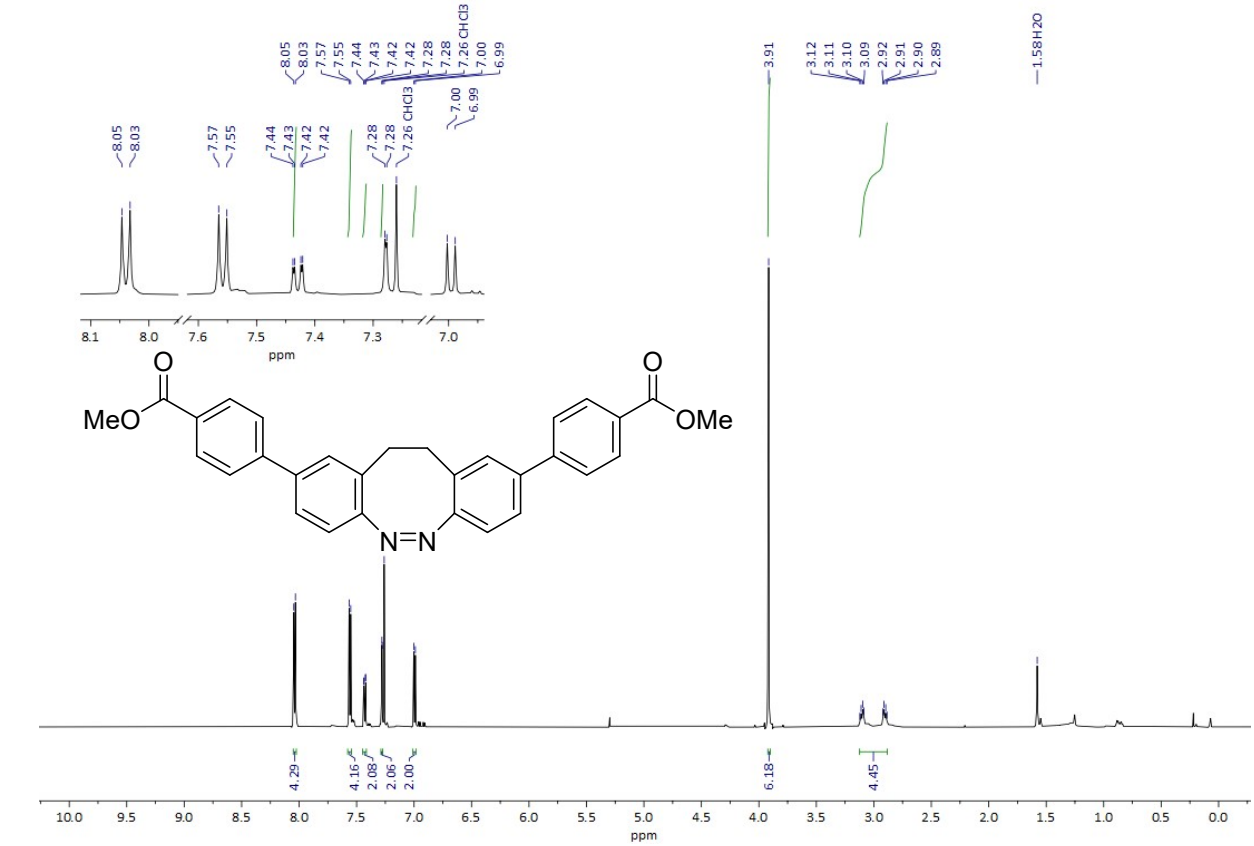


Figure 62: ^{1}H NMR spectrum of **23** in $CDCl_3$.

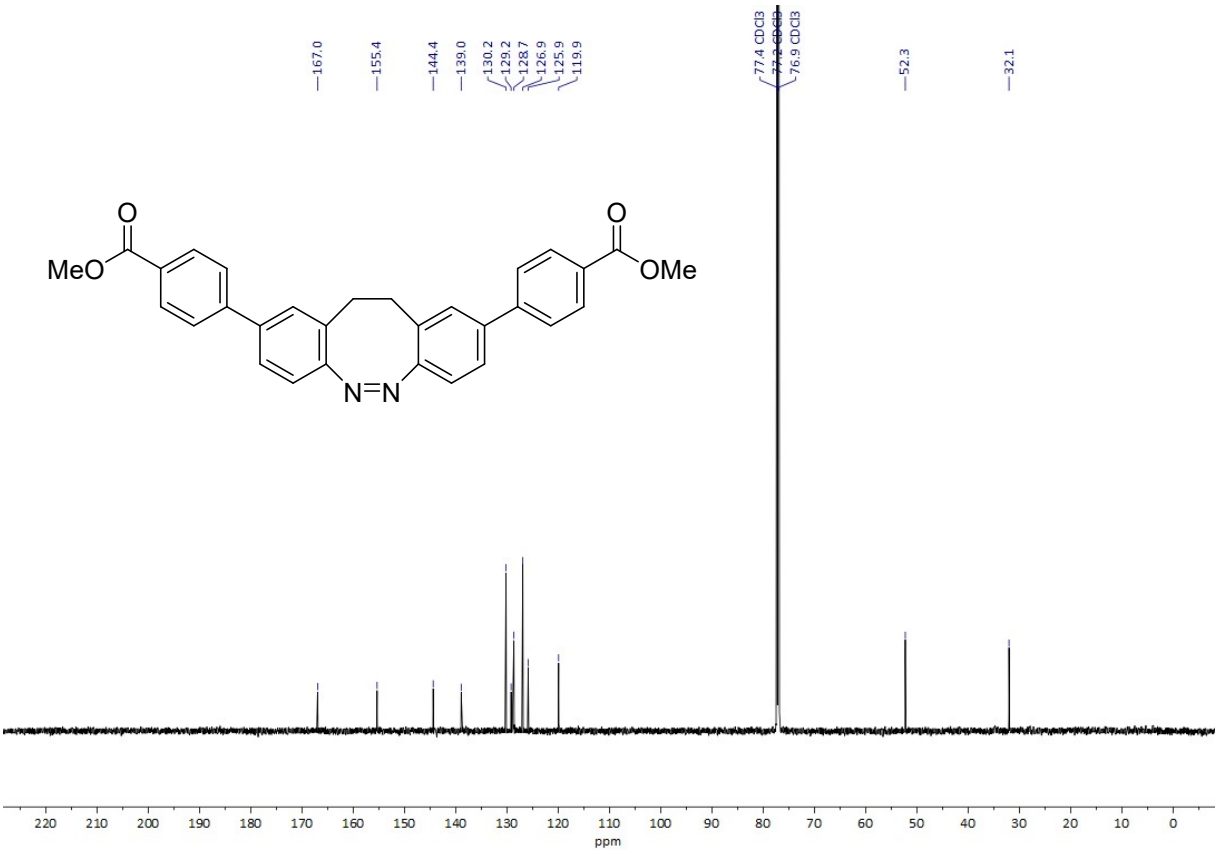


Figure 63: $^{13}C\{^{1}H\}$ NMR spectrum of **23** in $CDCl_3$.

(*Z*)-2,9-Bis(benzo[*d*][1,3]dioxol-5-yl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**24**)

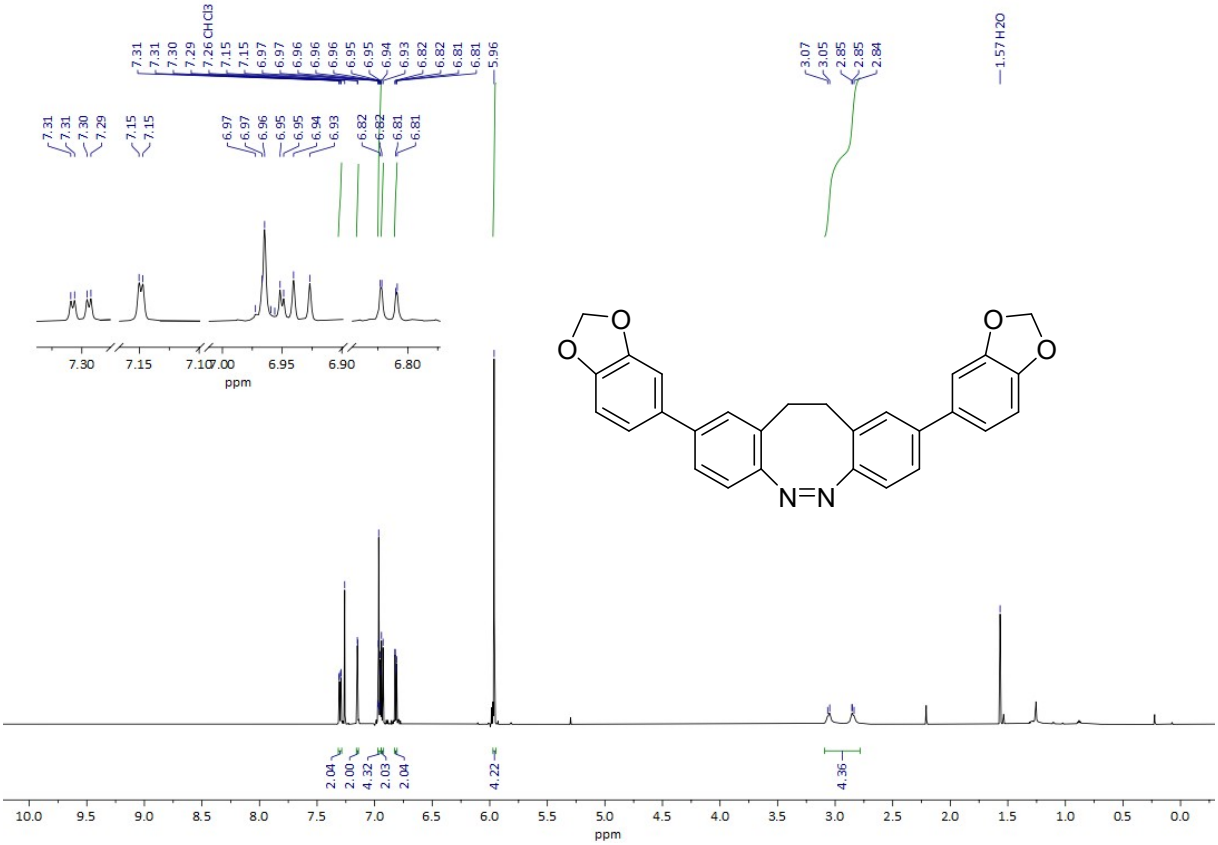


Figure 64: ^{1}H NMR spectrum of **24** in $CDCl_3$.

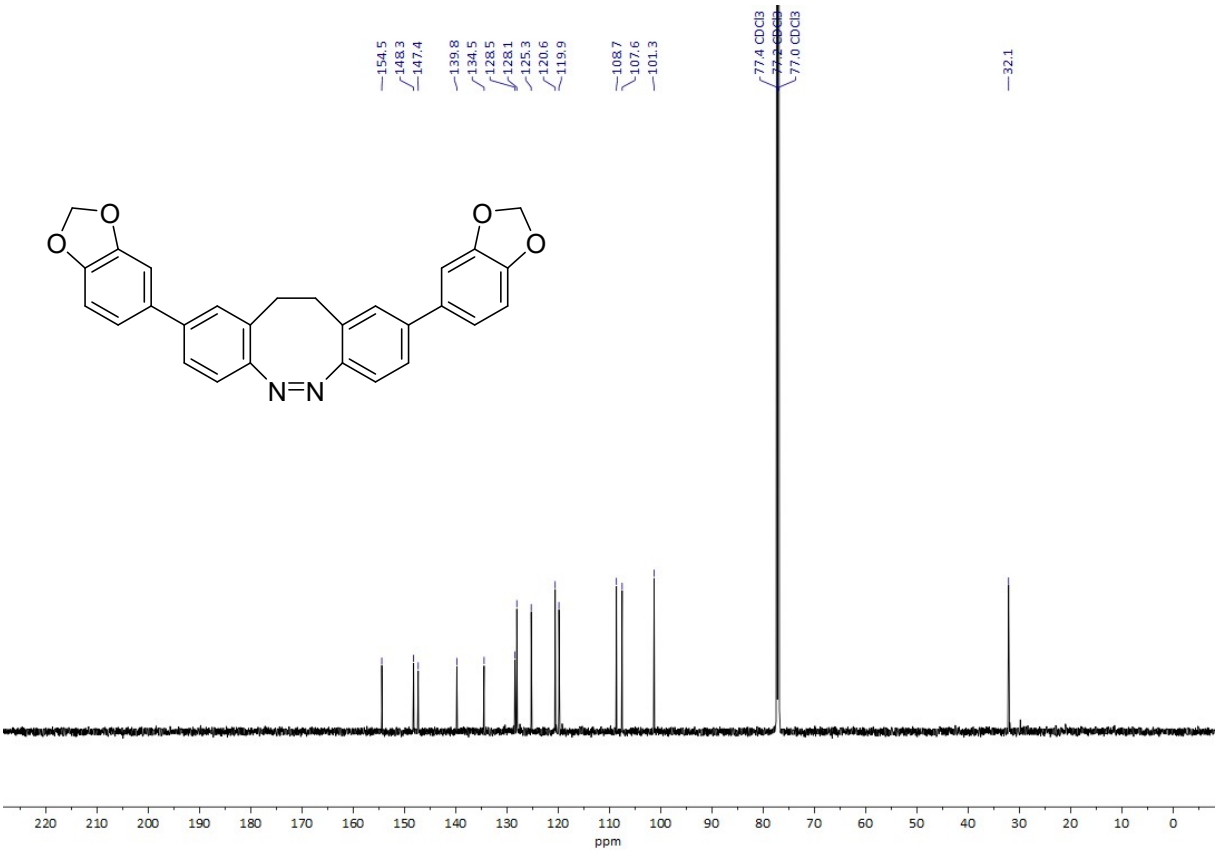


Figure 65: $^{13}C\{^{1}H\}$ NMR spectrum of **24** in $CDCl_3$.

(*Z*)-2,9-Di(thiophen-2-yl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**25**)

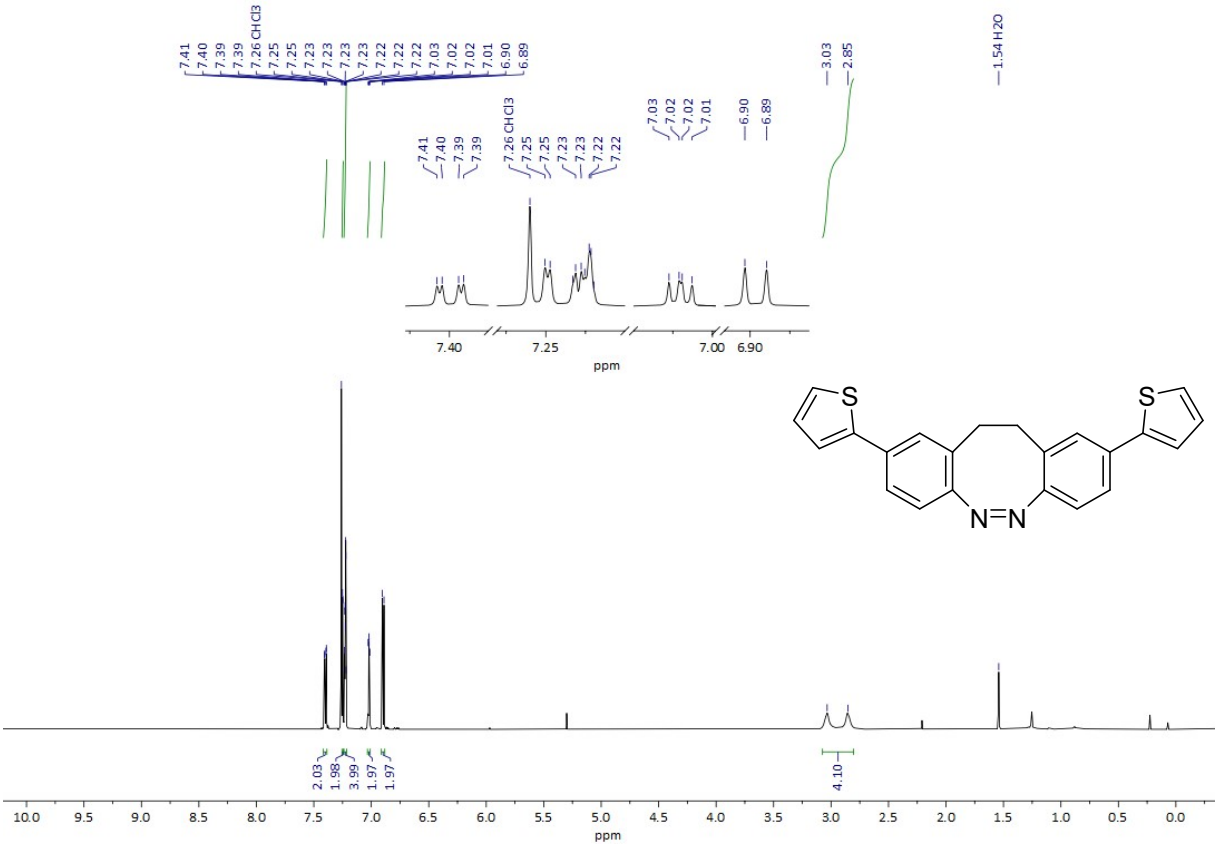


Figure 68: ^{1}H NMR spectrum of **25** in $CDCl_3$.

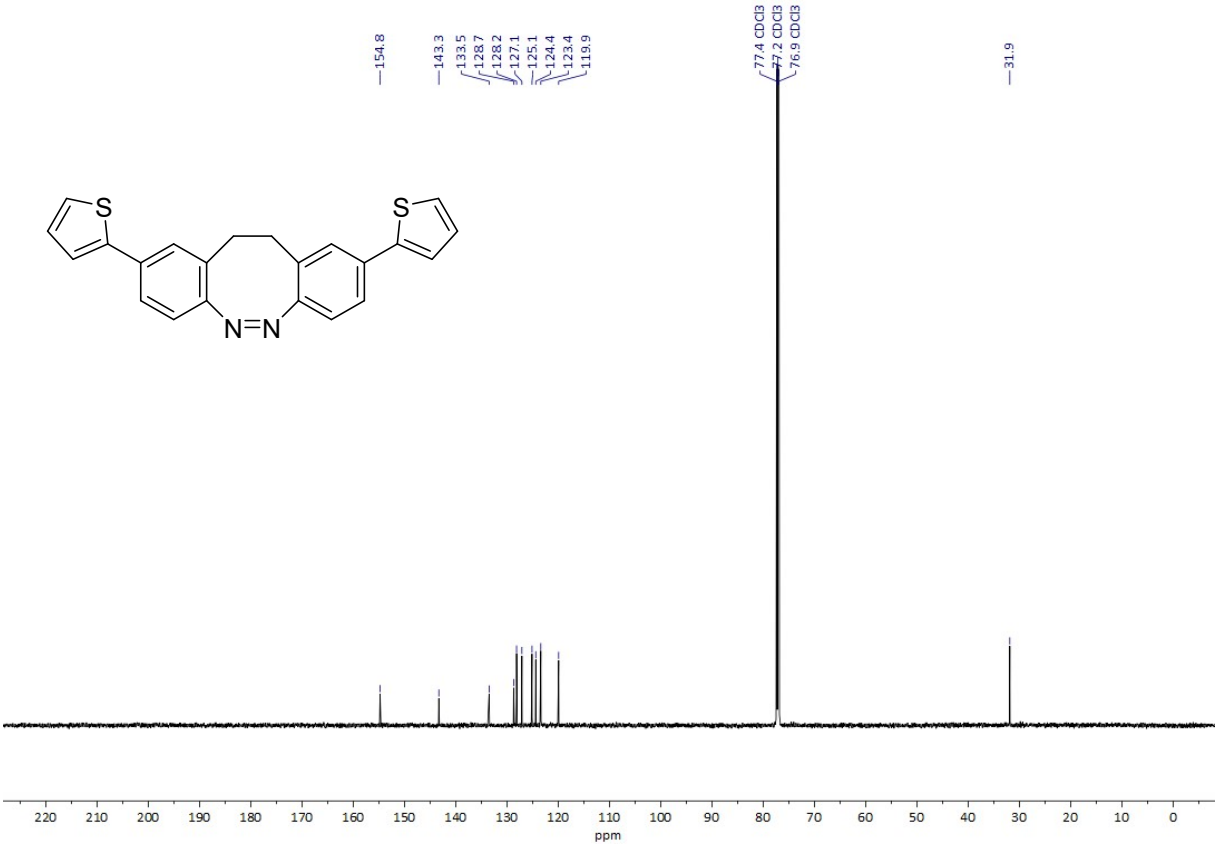


Figure 69: $^{13}C\{^{1}H\}$ NMR spectrum of **25** in $CDCl_3$.

(*Z*)-2,9-Di(thiophen-3-yl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**26**)

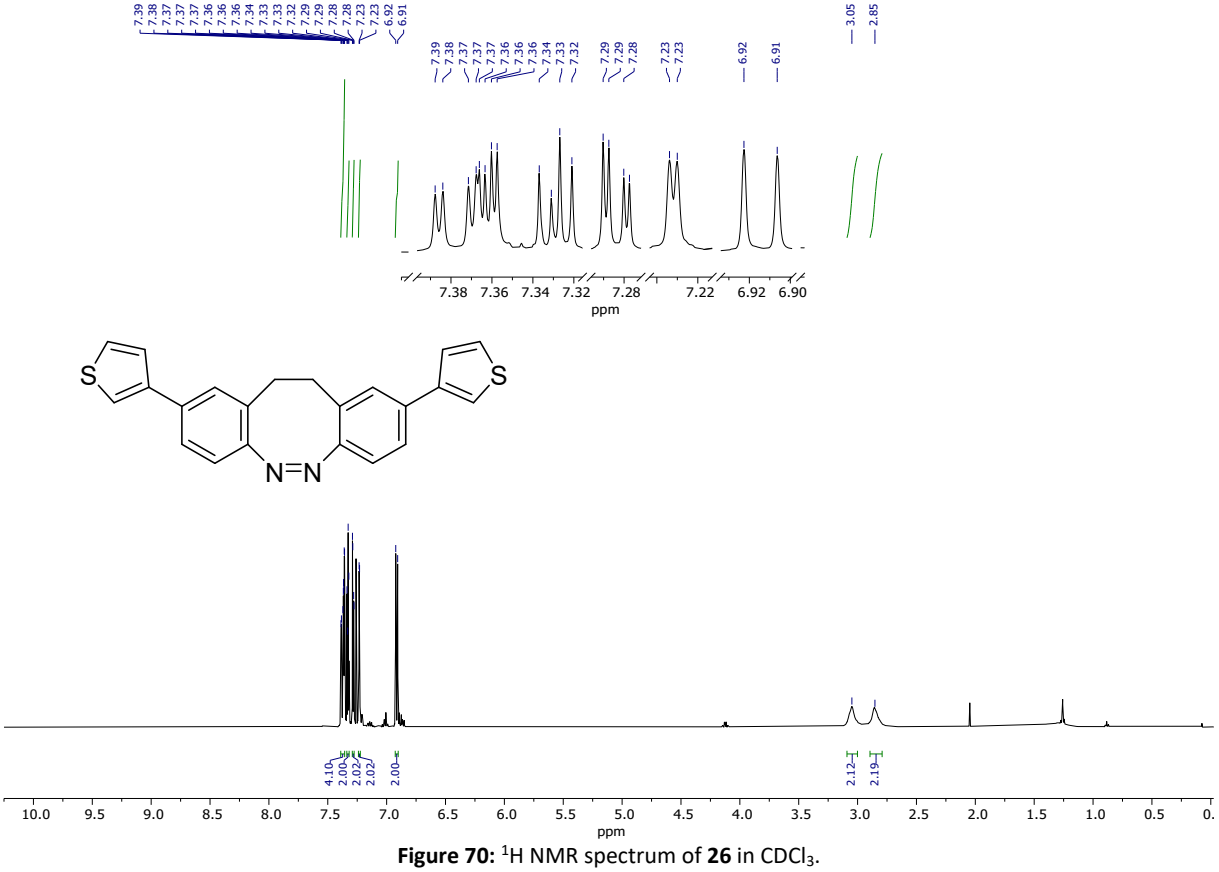


Figure 70: ^{1}H NMR spectrum of **26** in $CDCl_3$.

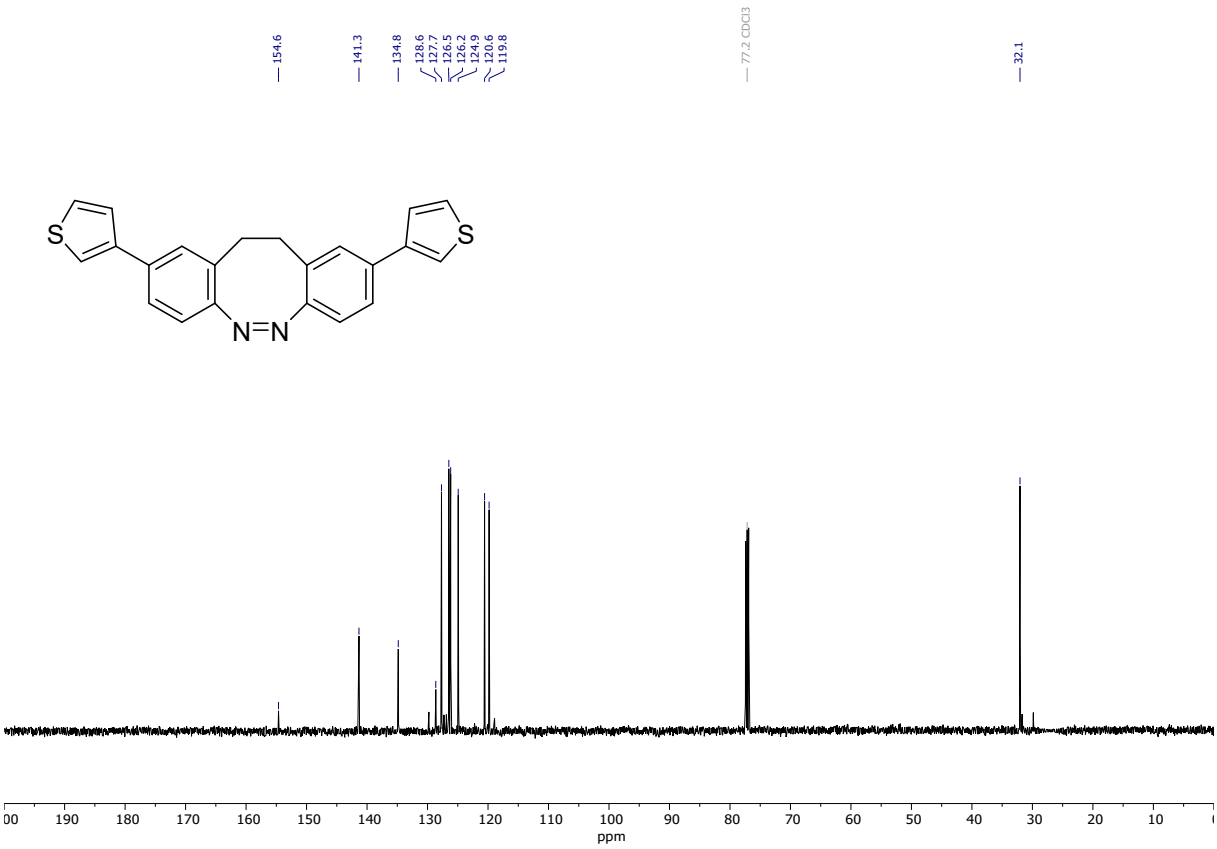


Figure 71: $^{13}C\{^{1}H\}$ NMR spectrum of **26** in $CDCl_3$.

(*Z*)-5,5'-(11,12-Dihydrodibenzo[*c*,*g*][1,2]diazocine-2,9-diyl)bis(furan-2-carbaldehyde) (**27**)

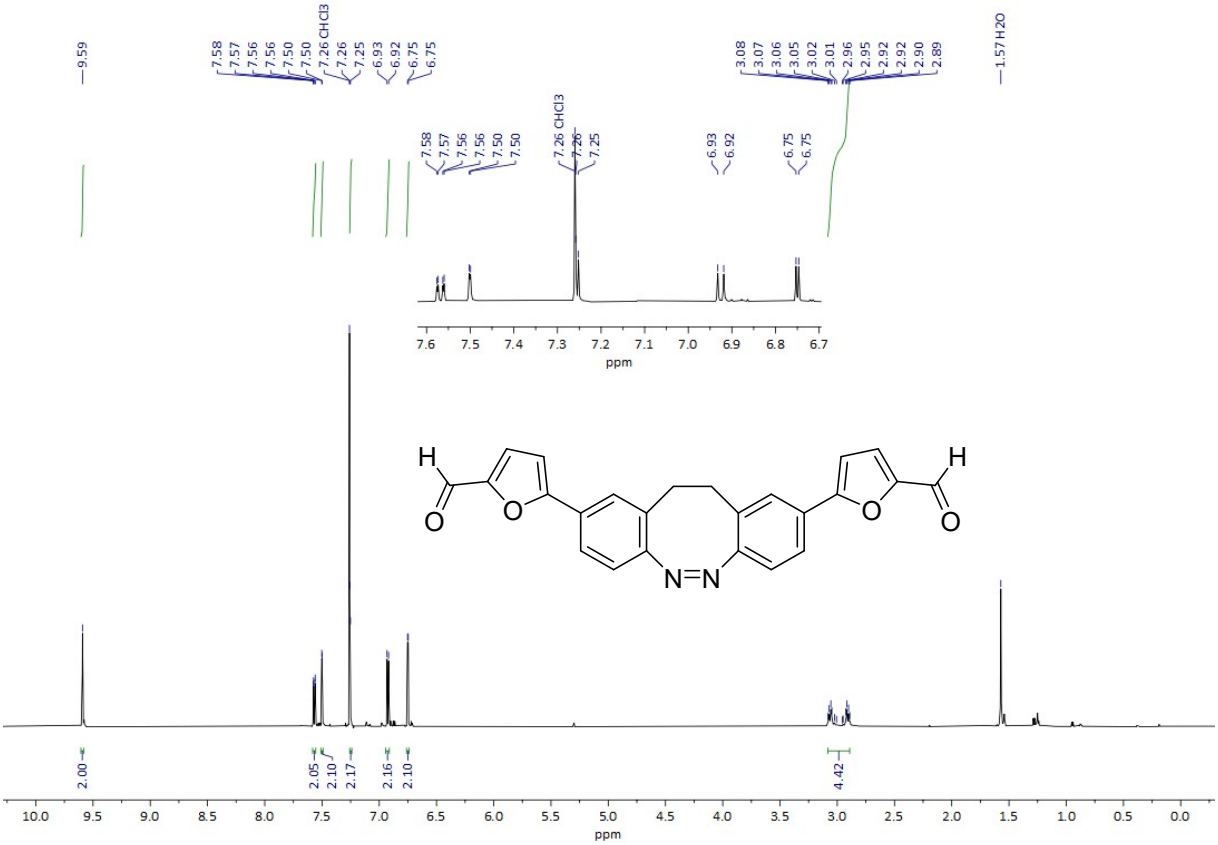


Figure 72: ^{1}H NMR spectrum of **27** in $CDCl_3$.

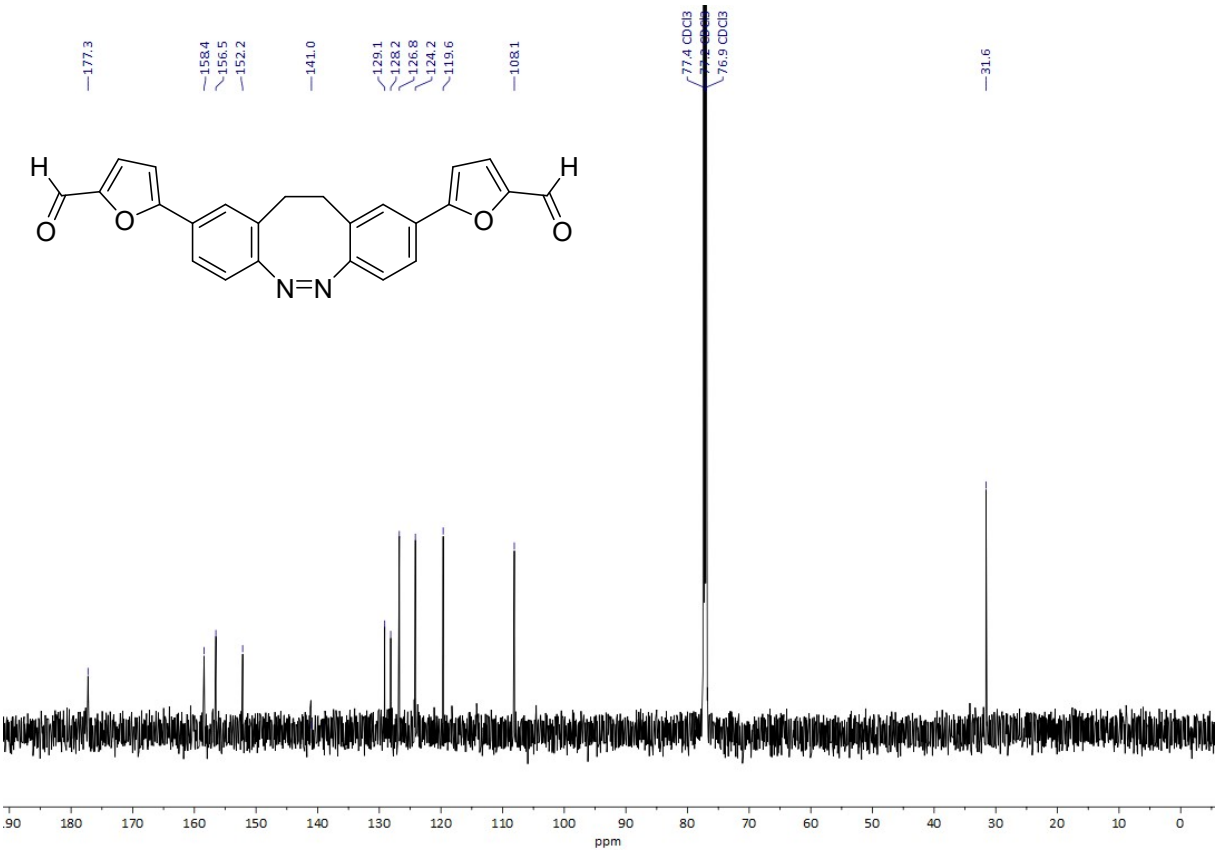


Figure 73: $^{13}C\{^{1}H\}$ NMR spectrum of **27** in $CDCl_3$.

Dimethyl 5,5'-(11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine-2,9-diyl)(*Z*)-bis(furan-2-carboxylate) (**28**)

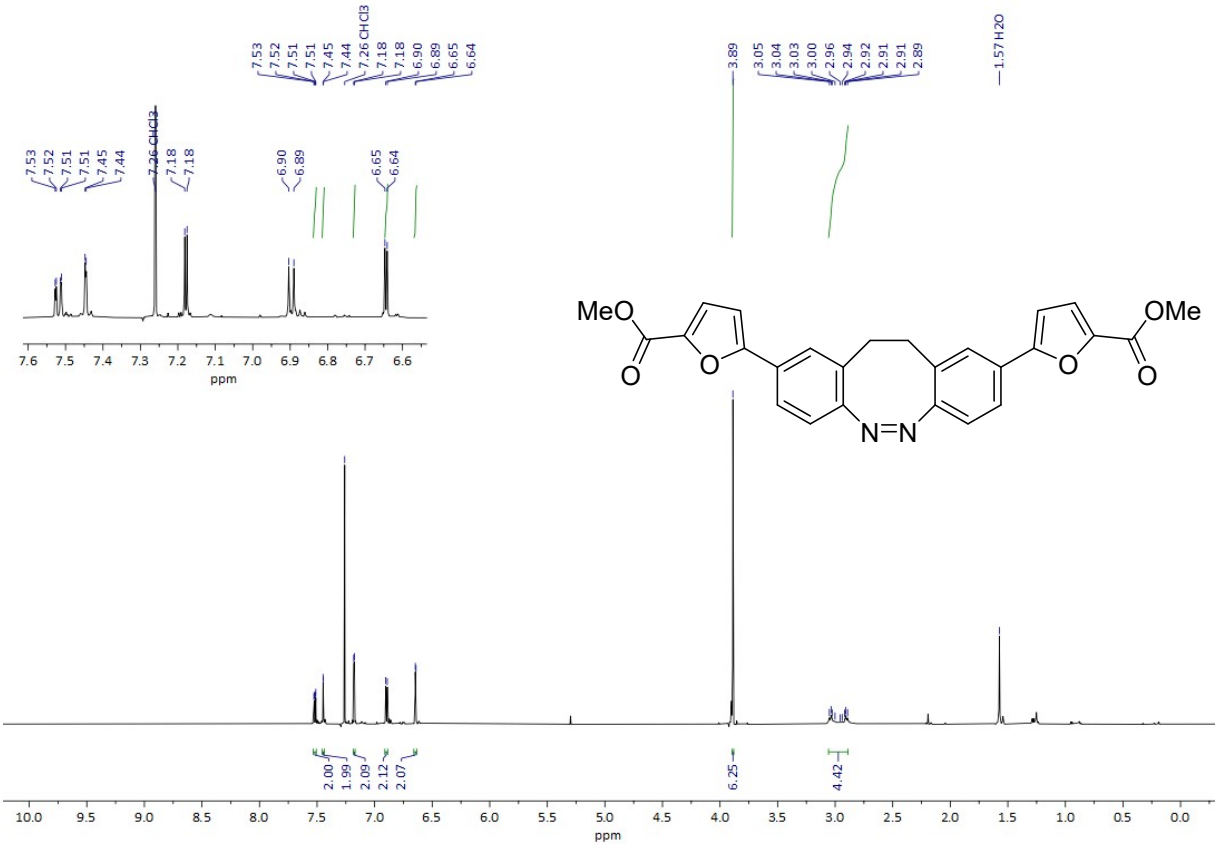


Figure 74: ^{1}H NMR spectrum of **28** in $CDCl_3$.

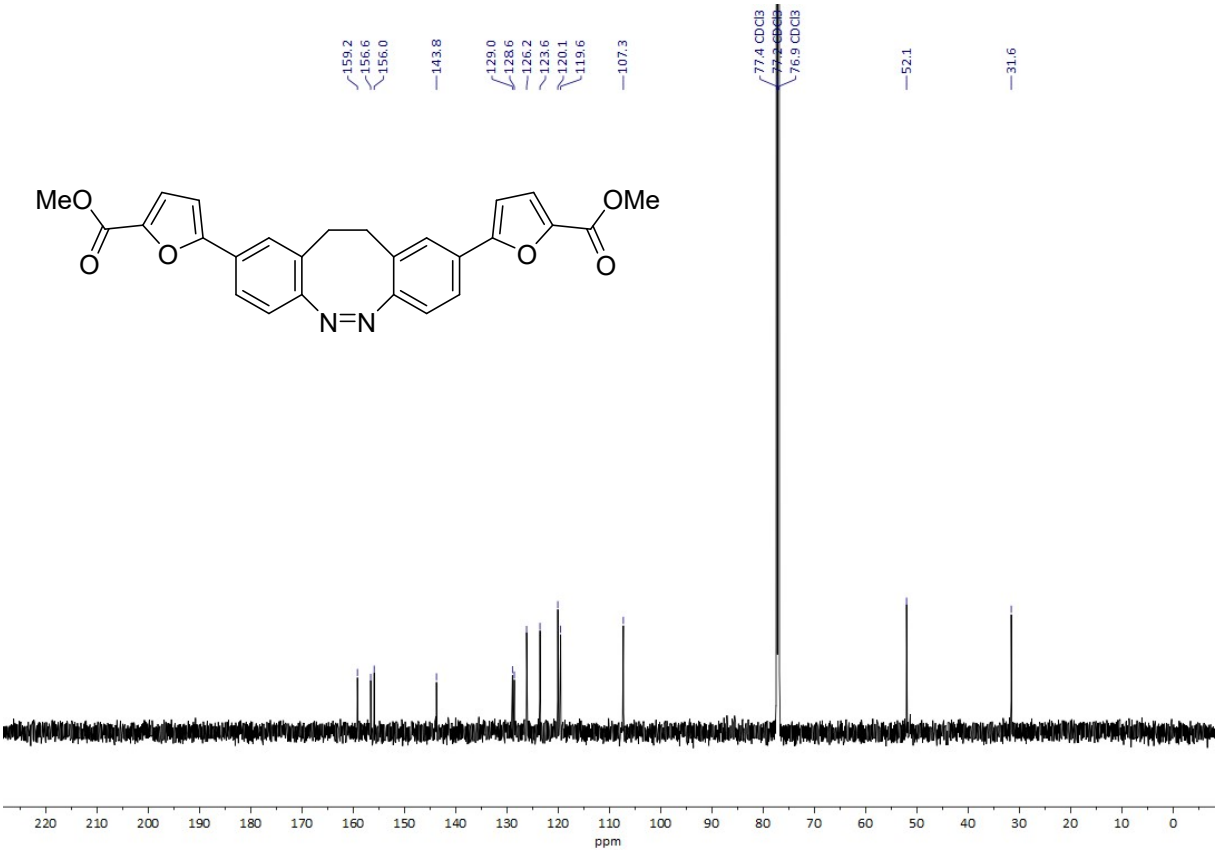


Figure 75: $^{13}C\{^{1}H\}$ NMR spectrum of **28** in $CDCl_3$.

(*Z*)-2,9-Di(pyridin-4-yl)-11,12-dihydrodibenzo*[c,g]*[1,2]diazocine (**29**)

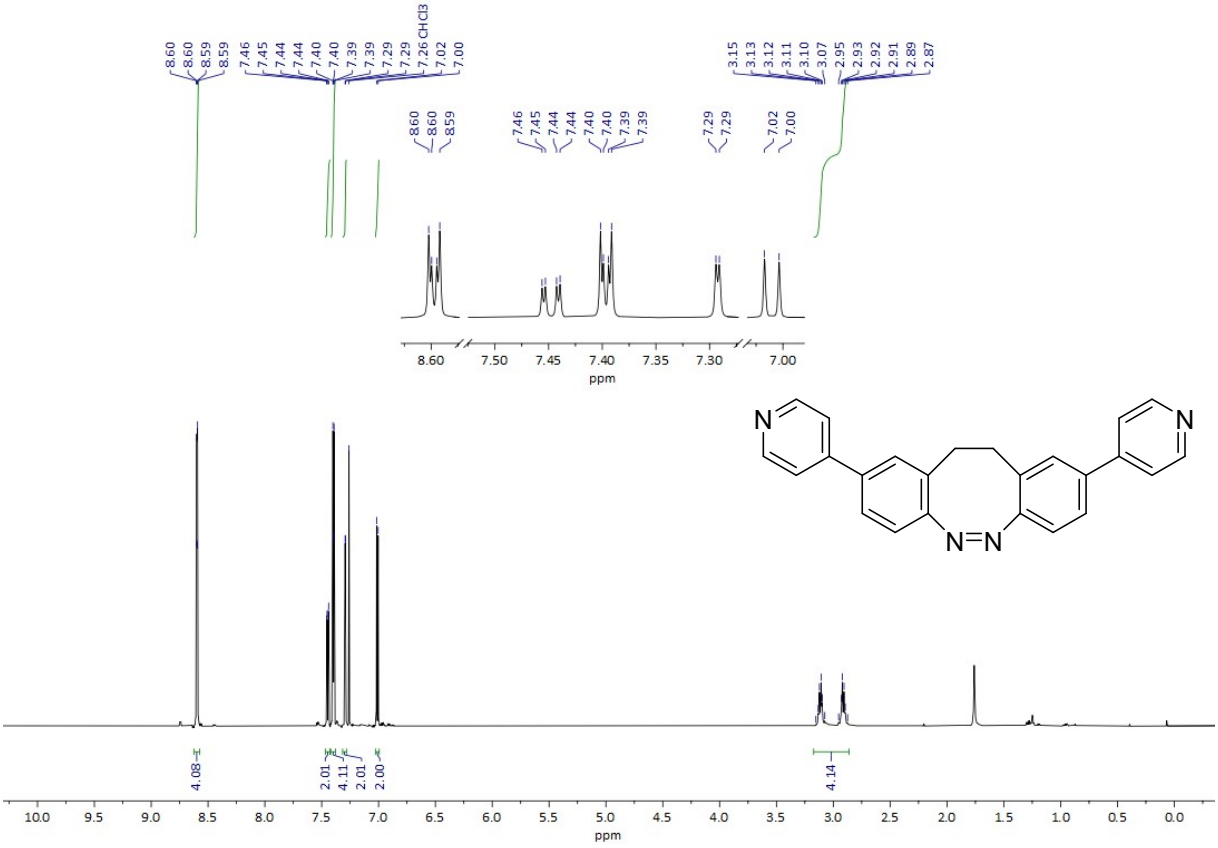


Figure 66: ^{1}H NMR spectrum of **29** in $CDCl_3$.

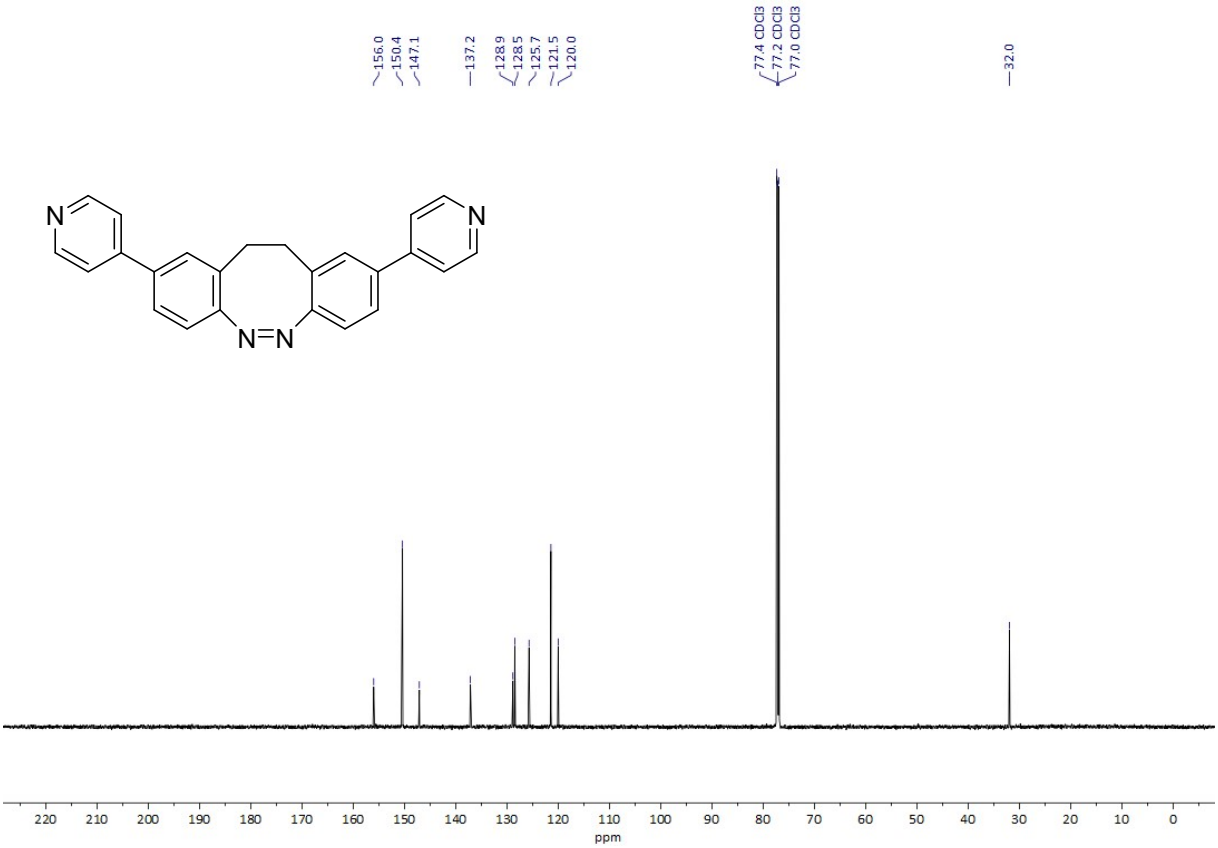


Figure 67: $^{13}C\{^{1}H\}$ NMR spectrum of **29** in $CDCl_3$.

(*Z*)-2,9-Diallyl-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**30**)

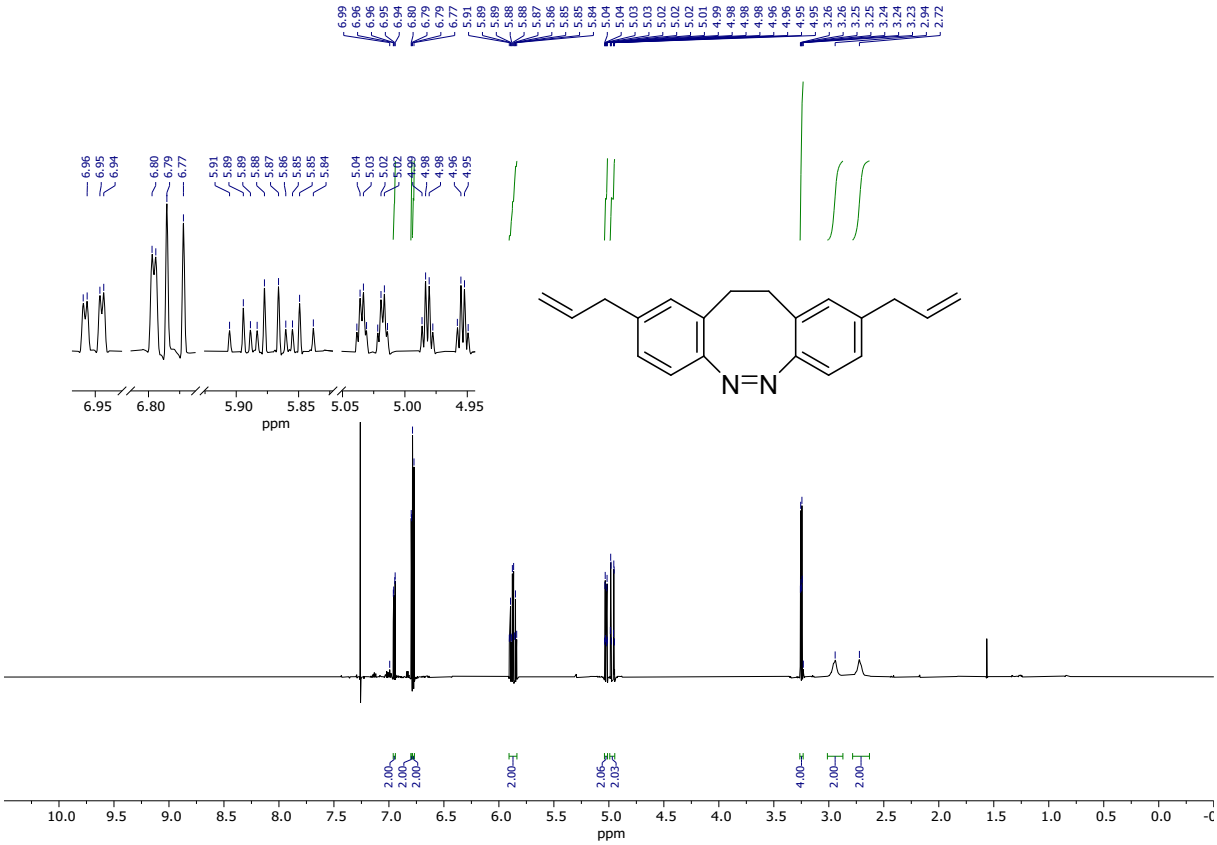


Figure 76: ^{1}H NMR spectrum of **30** in $CDCl_3$.

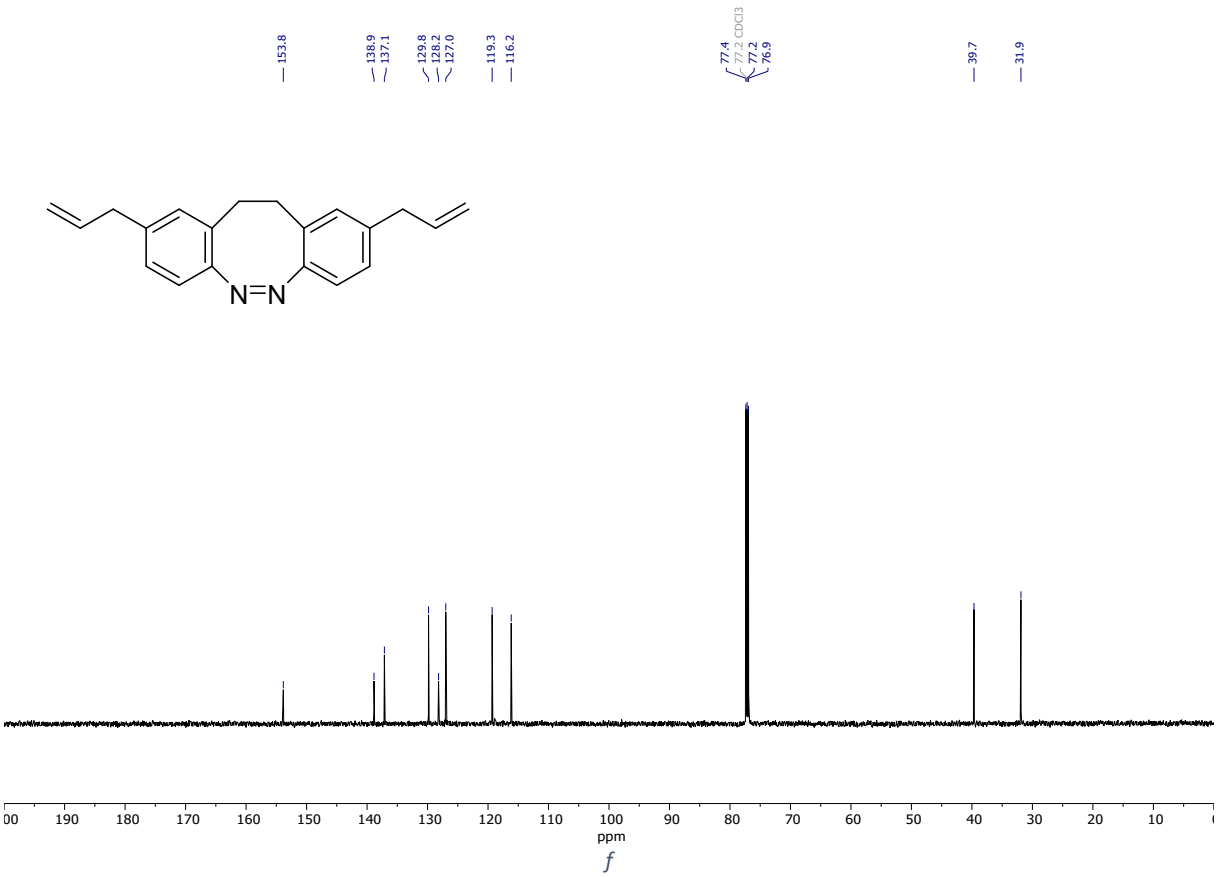


Figure 77: $^{13}C\{^{1}H\}$ NMR spectrum of **30** in $CDCl_3$.

(*Z*)-3,8-Di-*p*-tolyl-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**35**)

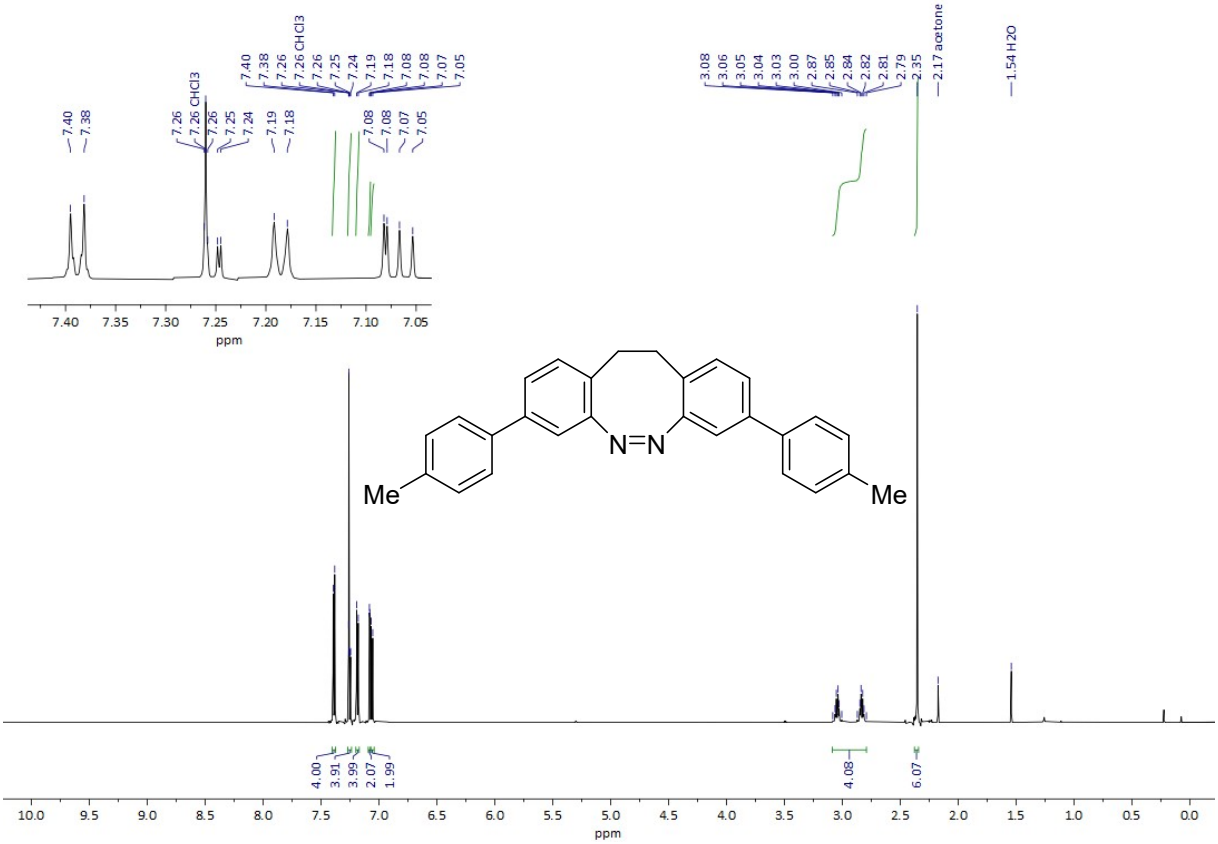


Figure 78: ^{1}H NMR spectrum of **35** in $CDCl_3$.

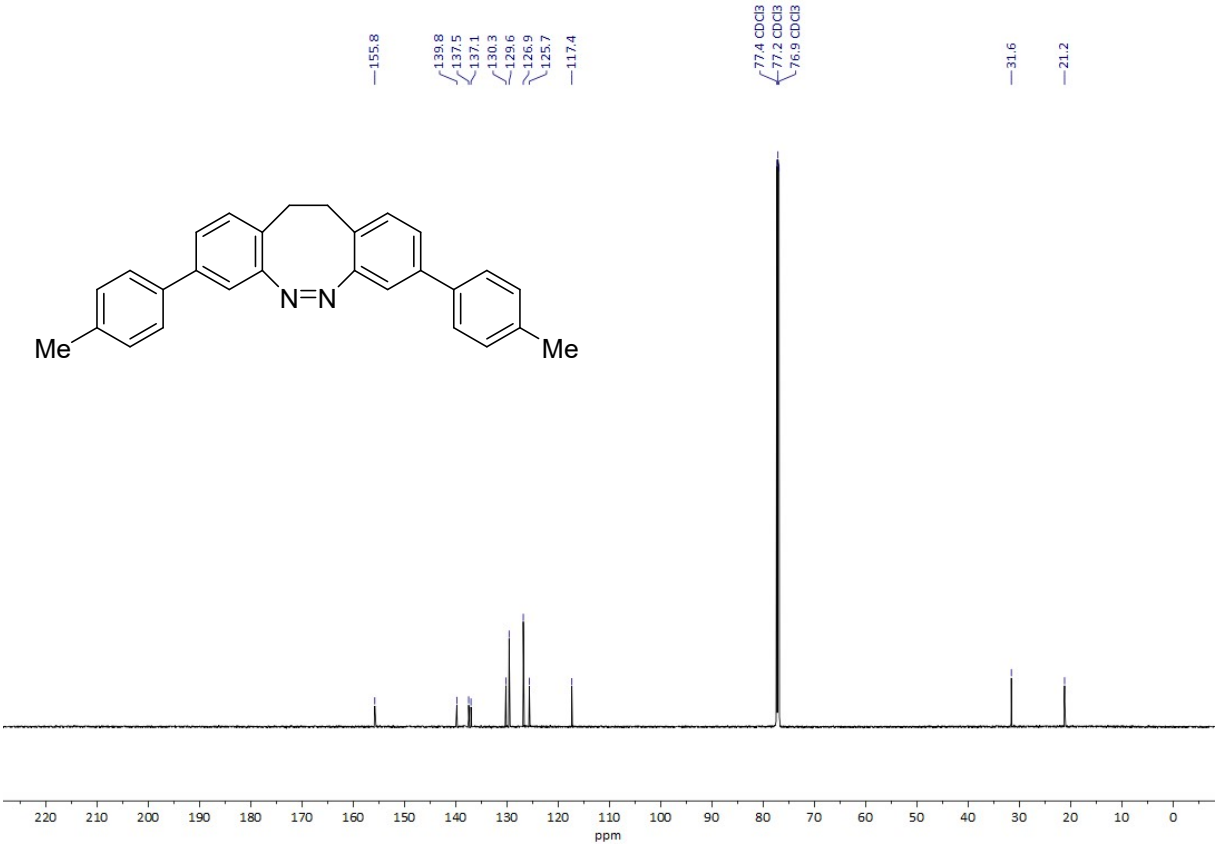


Figure 79: $^{13}C\{^{1}H\}$ NMR spectrum of **35** in $CDCl_3$.

(*Z*)-3,8-Bis(4-methoxyphenyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**36**)

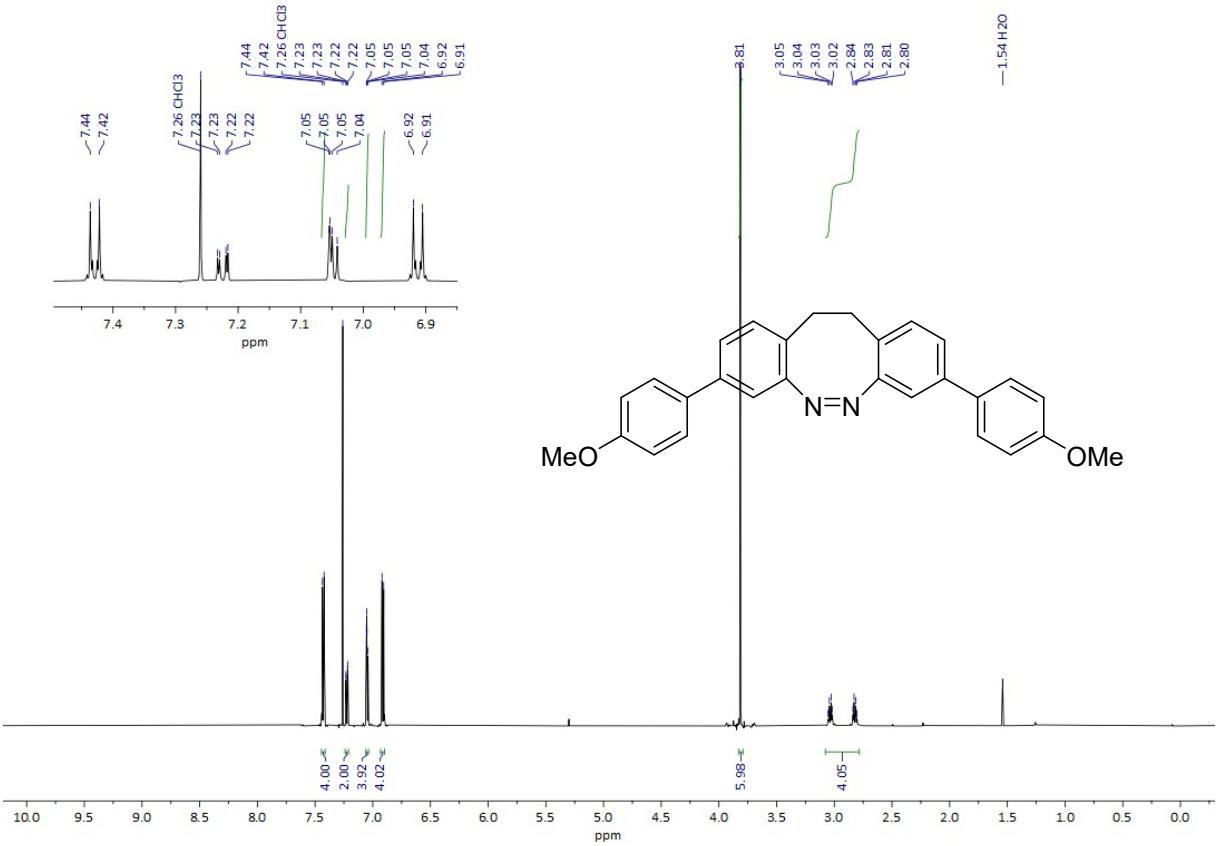


Figure 80: ^{1}H NMR spectrum of **36** in $CDCl_3$.

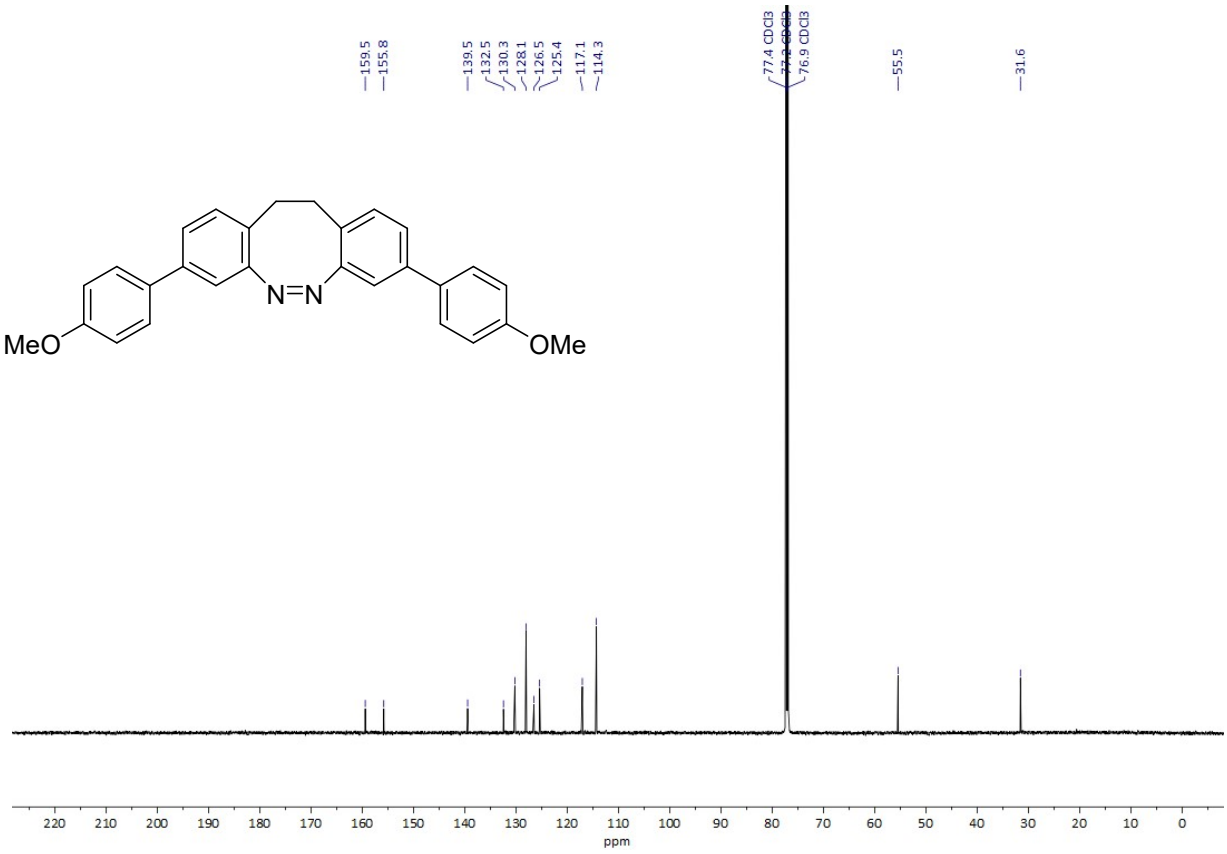


Figure 81: $^{13}C\{^{1}H\}$ NMR spectrum of **36** in $CDCl_3$.

(*Z*)-3,8-Bis(4-nitrophenyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**37**)

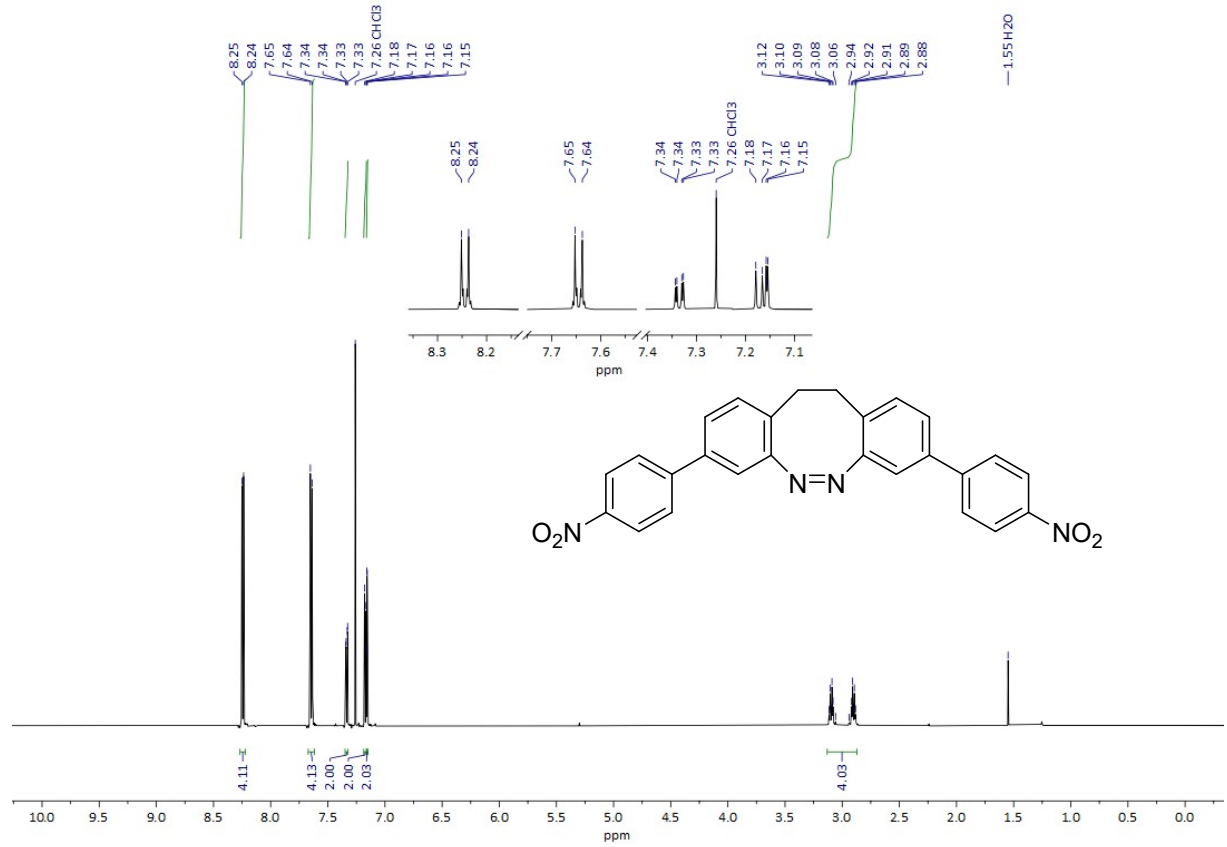


Figure 82: ^{1}H NMR spectrum of **37** in $CDCl_3$.

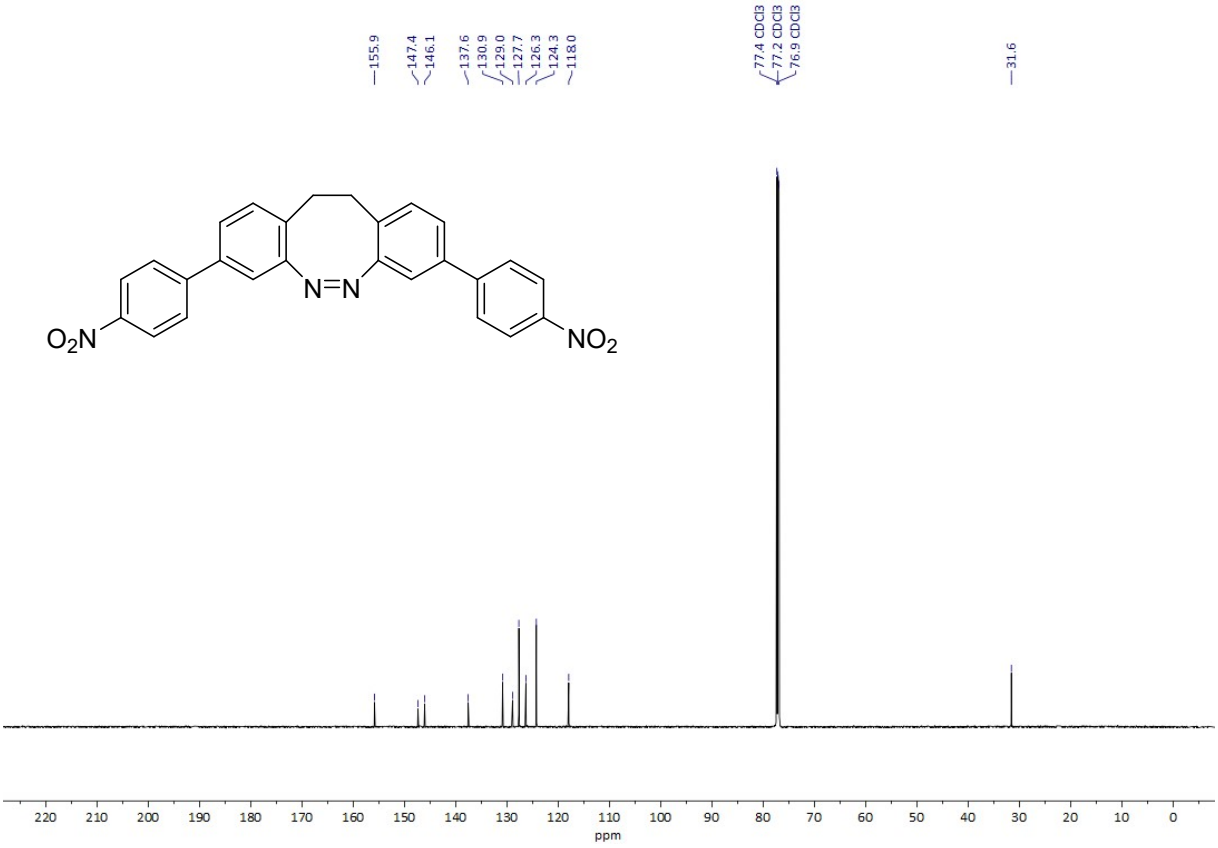


Figure 83: $^{13}C\{^{1}H\}$ NMR spectrum of **37** in $CDCl_3$.